Bifurcation analysis of chemical reaction mechanisms. 
II. Hopf bifurcation analysis

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One- and two-parameter Hopf bifurcation behavior is analyzed for several variants of the Citri–Epstein mechanism of the chlorite–iodide reaction. The coefficients of an equation for the amplitude of oscillations (the universal unfolding of the Hopf bifurcation) are evaluated numerically. Local bifurcation diagrams and bifurcation sets are derived from the amplitude equation. Sub- and supercritical Hopf bifurcations are identified for the general case of a nondegenerate (codimension one) bifurcation. At degenerate (codimension two) points, the necessary higher-order terms are included in the unfolding, and features such as locally isolated branches of periodic orbits and bistability of a periodic orbit and a steady state are found. Inferences about the global periodic orbit structure and the existence of nearby codimension three Hopf bifurcation points are drawn by piecing together the local information contained in the unfoldings. Hypotheses regarding the global periodic orbit structure are tested using continuation methods to compute entire branches of orbits. A thorough discussion of the application of these methods is presented for one version of the mechanism, followed by a comparison of the complete two-parameter steady state bifurcation structure of three versions of the mechanism. In all cases, the potential for experimental verification of the predicted dynamics is examined.

I. INTRODUCTION

Since Bray reported in 1921 that hydrogen peroxide decomposes in the presence of acidic iodate with an oscillatory rate, periodic behavior of reactions in homogeneous solution has received considerable attention. This phenomenon was viewed with much skepticism until a detailed reaction mechanism was proposed by Field, Körös, and Noyes for the Belousov–Zhabotinskii reaction some 50 years later. With the introduction of the continuous-flow stirred tank reactor (CSTR), a large number of new systems exhibiting sustained periodic behavior have been discovered in recent years, and elementary step mechanisms have been developed for a significant fraction of these new systems.

The basic data obtained from a CSTR kinetics experiment are the bifurcation diagram, which is a plot of a measured response variable as a function of a control parameter, and the bifurcation set, which is a plot of regions of distinct dynamics (e.g., multiple steady states, oscillatory behavior, etc.) as a function of two or more parameters. Due to the time-consuming nature of the experimental determination of a bifurcation set, all but two parameters are typically held constant. The resulting two-parameter bifurcation set is also known as a phase diagram. In order to test the fidelity of a proposed mechanism, bifurcation diagrams and bifurcation sets must be computed. The method usually adopted for these computations is numerical integration of the rate equations, which produces a series of concentrations at selected times. The widespread availability of robust algorithms makes this an attractive choice; on the other hand, one limitation is that bifurcations are not indicated directly, but rather must be inferred from the time series.

We advocated numerical bifurcation analysis of chemical reaction mechanisms as an alternative to numerical integration in the preceding paper in this series, and demonstrated there the efficacy of the method by computing and analyzing two-parameter steady state bifurcation sets (i.e., saddle-node and Hopf bifurcation curves) for mechanisms of the chlorite–iodide and mixed Landolt reactions. Although the steady state bifurcation structure reveals only part of the system's dynamics, discrepancies between experiment and model are often already apparent at this level of description. In this paper, we show how a general equation for the amplitude of periodic orbits near Hopf bifurcations gives information about periodic behavior. Since sustained periodic behavior in a CSTR is often due to a Hopf bifurcation, the location and characterization of this type of bifurcation is an essential step in the validation of a reaction mechanism. Furthermore, we are able to identify regions of parameter space in which a stable steady state and a stable periodic orbit coexist or in which a closed loop of periodic orbits is likely to be present. Predictions regarding such dynamics are not only of intrinsic interest, but also suggest stringent experimental tests of the mechanism.

Bifurcation to a limit cycle in a chemical reactor has been studied extensively in the chemical engineering literature. In a series of three papers, Aris and Amundson examined the stability of a CSTR under feedback control,
taking the strength of the feedback as the bifurcation parameter. General formulas for determining the direction and stability of the branch of orbits that bifurcate from the branch of steady states were applied to the first-order exothermic reaction in a CSTR without feedback control nearly 20 years ago. Results derived from the $n$-dimensional theory of Hopf for the Oregonator model of the Belousov-Zhabotinskii reaction. The CSTR with two consecutive reactions was investigated subsequently. The classification of degenerate Hopf bifurcations according to singularity theory has triggered much of the current computational effort. The results for two consecutive reactions in a CSTR were extended, and the effects of extraneous thermal capacitance on the dynamics of a CSTR with a first-order exothermic reaction were examined. Degenerate Hopf bifurcation behavior of the cubic autocatalator has been examined from the viewpoint of singularity theory as well. Some aspects of the Hopf bifurcation behavior of models of the Belousov-Zhabotinskii reaction have been analyzed recently by methods related to those used here; however, to the best of our knowledge, this paper is the first application of singularity theory to a Hopf bifurcation analysis of a chemical reaction mechanism derived directly from elementary step mass-action kinetics.

We have chosen the Citri-Epstein mechanism of the chlorite-iodide reaction to serve as the example in the analysis which follows. A better understanding of a wide variety of dynamical phenomena is likely to follow from improvements in the mechanism of this reaction owing to its role in a large number of nonlinear chemical systems. For example, the chlorite-iodide reaction in the presence of malonic acid provided the first experimental evidence of a Turing structure. Evidence of the relative maturity of the mechanism is given by the fact that the Citri-Epstein scheme is a second-generation mechanism designed to overcome limitations of an earlier set of reactions.

Both nondegenerate and degenerate Hopf bifurcations are analyzed. A bifurcation that occurs generically upon variation of a single parameter is nondegenerate; the codimension of such a bifurcation is one. To observe a degenerate bifurcation, two or more parameters must be varied; the minimum number of parameters so required is an operational definition of the codimension of a degenerate bifurcation. With this definition, the dimension of the set of parameters on which a bifurcation is observed is calculated by subtracting the codimension of the bifurcation from the dimension of the entire parameter space.

The analysis of a Hopf bifurcation is more involved than that of a saddle-node bifurcation. For a nondegenerate Hopf bifurcation, the stability of the resultant periodic orbit is not determined by the eigenvalues of the Jacobian at the bifurcation point, whereas the stability of the pair of steady states produced by a codimension one saddle node bifurcation is specified fully by the Jacobian's eigenvalue spectrum. Moreover, all codimension two saddle-node bifurcations impart a typical geometry to the bifurcation set. While certain degenerate Hopf bifurcations have a geometric signature, the codimension two Hopf bifurcation leading to multiple periodic orbits does not. Identification of the latter type of Hopf bifurcation is important because it is often responsible for the frequently observed situation in which stable large amplitude oscillations coexist with a stable steady state.

In Sec. II, multiparameter Hopf bifurcation theory is outlined. In the course of this overview, the basic equations and associated notation that appear in the remainder of the paper are introduced. The numerical methods are described briefly in Sec. III. A detailed exposition of the Hopf bifurcation behavior of the Citri-Epstein mechanism of the chlorite-iodide reaction is found in Sec. IV. The possibility of distinguishing between mechanisms on the basis of their steady state bifurcation sets is explored in Sec. V by comparing results for three variants of the Citri-Epstein mechanism. In the final section, some comments are offered on the role of degeneracies requiring more than two parameters in revealing relationships between mechanisms, and our results are summarized.

II. MULTIPARAMETER HOPF BIFURCATION THEORY

The dimension of the subset of parameter space on which a bifurcation occurs decreases as the bifurcation becomes more degenerate. For this reason, bifurcations of higher codimension are harder to observe. Based on this comment, one might conclude that studying such multiparameter bifurcations is not of practical interest. In many cases, however, a bifurcation set of codimension $n$ acts as an organizing center for bifurcation sets of codimension $n-1$ by virtue of being the intersection of the sets of lower codimension. Balakotaiah and Luss have demonstrated that finding the most degenerate saddle-node bifurcations is of great advantage in mapping the regions of steady state multiplicity. Similarly, useful insights into the structure of the bifurcation set result when the higher codimension bifurcations of periodic orbits are viewed as organizing centers. Taken together, this paper and its predecessor describe methods that generate a complete two-parameter description of the steady state bifurcation structure. In their role as organizing centers, one of the Hopf bifurcations to be discussed below and the Takens-Bogdanov bifurcation that results when a curve of Hopf points terminates on a curve of saddle-node bifurcations allow us to take a step towards filling in the periodic orbit bifurcation structure as well.

A rigorous definition of universal unfolding requires more mathematical precision than is necessary for our purposes. Conceptually, the universal unfolding is the minimal set of equations that retains all the qualitative dynamics exhibited by the system for parameter values near the bifurcation point. It is minimal with respect to both the number of variables and the number of parameters it requires. For this reason, it is convenient to derive bifurcation diagrams and sets for the unfolding rather than for the complete system of equations. Using the fact that the qualitative behaviors are the same, the dynamics deduced for the unfolding can be related to those of the original system.
The interested reader can find excellent treatments of bifurcation theory in several recent monographs. With this in mind, we intend for this section to introduce multiparameter Hopf bifurcation theory at a heuristic level to those not acquainted with the subject. We hope the outline presented here contains enough detail to make the arguments plausible and to motivate the subsequent application of the theory to a chemical reaction mechanism. For readers already familiar with the subject, this section need only be scanned so that the notation of the following sections is clear.

The nonlinear ordinary differential equations to be studied here are derived from the rate equations of mass-action chemical kinetics. For a reaction mechanism with \( N \) chemical species and \( M \) parameters (reaction constants, mass flow rates, feed stream concentrations, etc.), we denote the species by \( \chi_j \) (\( j=1,2,...,N \)) and the parameters by \( \lambda_i \) (\( i=1,2,...,M \)). In vector notation, the rate equations for a CSTR have the form

\[
\dot{x} = f(x, \lambda).
\]

The function \( f \) consists of the reaction rate expressions, a term for the inflow of unreacted material into the CSTR, and a term for the outflow of the contents of the reactor at a rate equal that of the inflow. If \((\bar{x}, \bar{\lambda})\) is a steady state, then

\[
\dot{x} = 0 = f(x, \lambda).
\]

A small-amplitude periodic orbit about the steady state results if the steady state undergoes a generic Hopf bifurcation. Taking \( \lambda_1 \) as the free parameter and fixing the remaining components of \( \lambda \), a Hopf bifurcation occurs as \( \lambda_1 \rightarrow \bar{\lambda}_1 \) varies from negative to positive provided that

(H1) \( J(x, \lambda) \) (the Jacobian of \( f \) with respect to \( x \)) has a pair of complex conjugate eigenvalues \( \sigma(\lambda) \pm i\omega(\lambda) \) satisfying \( \sigma(\bar{\lambda}_1) = 0 \) and no other eigenvalues of \( J \) have zero real part at \((\bar{x}, \bar{\lambda})\);

(H2) the pair of complex conjugate eigenvalues crosses the imaginary axis such that

\[
\left. \frac{\partial \sigma}{\partial \lambda_1} \right|_{\lambda = \bar{\lambda}} \neq 0;
\]

(H3) in the equation for the amplitude \( r \) of the periodic orbits

\[
\dot{r} = r [a_0(\lambda) + a_1(\lambda) r^2 + a_2(\lambda) r^4 + \cdots],
\]

the coefficient \( a_1 \) is not zero at \( \lambda = \bar{\lambda} \).

Equation (3) is the universal unfolding of the Hopf bifurcation. Since \( r \) is the radius of the periodic orbit, solutions for which \( r < 0 \) are unphysical and are not included in the analysis. While \( r \) can be related to the variables of the system, we have not attempted to do this for the reaction mechanisms to be discussed, so \( r \) should be thought of as the radius of a schematic periodic orbit. \( a_i \) are the unfolding coefficients. The unfolding is written in this form to emphasize that the coefficients are functions of the natural parameters \( \lambda \) of the problem. To associate the dynamics predicted by the unfolding with regions in the natural parameter space, the dependence of \( a_i \) on \( \lambda \) must be known at least approximately. It should be emphasized at this point that universal unfolding theory is inherently local in nature. The unfolding equation is only valid in a neighborhood of the bifurcation point and \( a \) priori estimates of the size of this neighborhood are generally not available.

The exceptional situations in which either \( a_0 = \partial \sigma / \partial \lambda_1 = 0 \) or \( a_0 = a_1 = 0 \) are precluded by hypotheses (H2) and (H3). These situations are exceptional because the theorem is stated for a one-parameter family of equations. If there are two free parameters, then, in either case, there are two equations in two unknowns and the existence of a \((\lambda_1, \lambda_2)\) pair at which hypothesis (H2) or (H3) fails to hold would not be unusual, as will be seen in Sec. IV.

For notational convenience, explicit indication of the dependence of the \( a_i \) on \( \lambda \) will be omitted whenever possible. A further simplification in notation follows from translation of the steady state \((\bar{x}, \bar{\lambda})\) to \((0,0)\). All partial derivatives of \( a_i \) with respect to \( \lambda_j \) are evaluated at the bifurcating steady state.

A. One- and two-parameter universal unfoldings

The universal unfolding of Eq. (3) can be derived from the vector field of Eq. (1) using center manifold theory. The center manifold is a surface that is invariant with respect to the vector field. The eigenvectors corresponding to the pair of pure imaginary eigenvalues are tangent to the center manifold at the bifurcating steady state. We assume that all remaining eigenvalues of the Jacobian have negative real parts. Under this assumption, the asymptotic dynamics are restricted to the center manifold, as all nearby trajectories are attracted to it at an exponential rate. It is this separation in time scales which allows for the reduction in dimension of the problem. If this assumption is not made, the periodic orbit resulting from the bifurcation is experimentally unobservable owing to unstable directions that are independent of the nature of the Hopf bifurcation. Because two eigenvalues have zero real part at the bifurcation point, the center manifold of the Hopf bifurcation is two dimensional. It is found that by writing the equations for the center manifold dynamics in polar form, the equation for the amplitude of the periodic orbit is decoupled from the equation for the orbit's frequency. The time evolution of the radial coordinate is given by Eq. (3); the angular coordinate is a constant rotation governed by \( \dot{\theta} = \omega(0) \) to lowest order. Other methods may be used to accomplish the reduction in dimension; regardless of the method used, a single equation of the form of Eq. (3) for the amplitude of the periodic orbits results.

To express the universal unfolding in terms of the natural parameters, \( a_i \) that vanish at the bifurcation point are expanded in power series in the desired components of \( \lambda \). In the final form of the unfolding, the series expansions for the coefficients are written only to lowest order since the analysis is done near the bifurcation point. In the notation of Ref. 20, the generic Hopf bifurcation described by the above theorem is labeled \( H_{00} \). If either of the hypotheses...
TABLE I. Universal unfoldings for the $H_{00}$, $H_{01}$, and $H_{10}$ Hopf bifurcations.

<table>
<thead>
<tr>
<th>Bifurcation</th>
<th>Universal unfolding</th>
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<tbody>
<tr>
<td>$H_{00}$</td>
<td>$r = r(a_0/\partial_{\lambda_1} + a_1 \lambda_1)$ (1.1)</td>
</tr>
<tr>
<td>$H_{01}$</td>
<td>$r = \left[ \frac{1}{2} \frac{\partial^2 a_0}{\partial \lambda_1^2} + \frac{\partial a_0}{\partial \lambda_2} \lambda_2 + a_1 r^2 \right]$ (1.2)</td>
</tr>
<tr>
<td>$H_{10}$</td>
<td>$r = \left[ \frac{\partial a_0}{\partial \lambda_1} + a_1 + \left( \frac{\partial a_0}{\partial \lambda_1} + \frac{\partial a_0}{\partial \lambda_2} \lambda_2 \right)^2 + a_1 r^2 \right]$ (1.3)</td>
</tr>
</tbody>
</table>

(H2) or (H3) is violated, a Hopf bifurcation of codimension two results as long as an additional condition (stated below in the discussion of the individual scenarios) is satisfied. A Hopf bifurcation of codimension two arising from violation of hypothesis (H2) is denoted by $H_{01}$; $H_{10}$ denotes the bifurcation at which hypothesis (H3) does not hold.

To second order,

$$a_0(\lambda_1, \lambda_2) = a_0(0,0) + \frac{\partial a_0}{\partial \lambda_1} \lambda_1 + \frac{\partial a_0}{\partial \lambda_2} \lambda_2 + \frac{1}{2} \frac{\partial^2 a_0}{\partial \lambda_1^2} \lambda_1^2 + \frac{1}{2} \frac{\partial^2 a_0}{\partial \lambda_2^2} \lambda_2^2.$$ (4)

It can be shown that $a_0 = \sigma$. Since $\sigma = 0$ at the bifurcation point, it follows that $a_0(0,0) = 0$. For the $H_{00}$ bifurcation, $\lambda_1$ is the free parameter; $\lambda_2$ is fixed at zero, so terms in Eq. (4) involving $\lambda_2$ are identically zero. Using the fact that $a_0 = \sigma$, hypothesis (H2) implies that the partial derivative of $a_0$ with respect to $\lambda_1$ is nonzero at the bifurcation point. Therefore, the series expansion of $a_0$ can be truncated after the linear term in $\lambda_1$. $a_1$ is nonzero by hypothesis (H3), so this coefficient is not expanded in a power series and the higher-order terms in $r$ are ignored. The resulting unfolding is Eq. (1.1) in Table I.

In the case of the $H_{01}$ bifurcation, a distinguished parameter must be designated since the partial derivative in hypothesis (H2) is taken with respect to a particular $\lambda_1$. Without loss of generality, $\lambda_1$ will be taken as the distinguished parameter and $\lambda_2$ will serve as the auxiliary unfolding parameter. Hypothesis (H2) is replaced by the hypothesis $\frac{\partial a_0}{\partial \lambda_1} \neq 0$. Thus, the lowest-order term in $\lambda_1$ of Eq. (4) is quadratic. Given only two free parameters, the other coefficients are generically nonzero. Therefore, the leading term in $\lambda_2$ is linear. $a_1$ is not expressed in power series form because hypothesis (H3) still applies. The universal unfolding in this case is given by Eq. (1.2).

For the $H_{10}$ bifurcation, hypothesis (H2) is valid while hypothesis (H3) is not. Hypothesis (H3) is replaced by the hypothesis $a_2 \neq 0$. Both $a_0$ and $a_1$ must be expanded. There is no distinguished parameter in the statement of hypothesis (H3), however. The constant term in the $a_1$ series is identically zero for reasons similar to those given for $a_0(0,0)$. All partial derivatives of $a_1$ and $a_2$ are nonzero if exceptional cases are excluded, so both unfolding coefficients can be expressed as linear functions of $\lambda_1$ and $\lambda_2$. This leads to Eq. (1.3) for the universal unfolding.

B. Bifurcation diagrams for one- and two-parameter unfoldings

As mentioned in the Introduction, the eigenvalue spectrum of the Jacobian at the Hopf bifurcation point is unrelated to the stability of the resultant periodic orbit. A linear stability analysis of the fixed points of the amplitude equation is required in order to assess the stability of the periodic orbit. As convenience dictates, one can use either the general form of Eq. (3) or a specific equation from Table I for this purpose. Solutions of $r = 0$ ($r > 0$) correspond to periodic orbits. Note that these equations contain only odd powers of $r$. As a consequence, $r = 0$ is always a solution of $r = 0$. This limit cycle of zero amplitude is known as the trivial solution and it corresponds to the steady state of the full problem.

The first step in determining an $(r, \lambda_1)$ bifurcation diagram is a stability analysis of the steady state. In two-parameter unfoldings, the sign of $\lambda_2$ must be fixed and a full description of the dynamics consists of two $(r, \lambda_1)$ bifurcation diagrams, one for $\lambda_2 > 0$ and one for $\lambda_2 < 0$. The linearization of Eq. (3) is

$$\frac{d\lambda}{dr} = a_0 + 3a_1 \lambda^2 + 5a_2 \lambda^4 + \cdots.$$ (5)

Upon substitution of $r = 0$ into this equation, only $a_0$ remains. By hypothesis (H1), $a_0$ changes sign (and the steady state changes stability via a Hopf bifurcation) as $\lambda_1$ passes through zero. Next, the possibility of nontrivial solutions to $r = 0$ is checked. If such solutions are found, the analysis is completed by computing their stability. The results of this procedure for the three unfoldings of Table I are given in Table II. The steady state is stable (a Hopf bifurcation point), or unstable depending on whether the Hopf bifurcation function is negative, zero, or positive. A periodic orbit (if it exists) is stable (a periodic orbit saddle node), or unstable depending on whether the periodic orbit stability function is negative, zero, or positive.

Representative local bifurcation diagrams are found in Fig. 1. At least one stable state must exist at a given parameter value; in cases for which only unstable states are shown in the figure, the existence of a stable state not associated with the bifurcation in question is understood. Figures 1(a) and 1(b) illustrate the basic Hopf bifurcation phenomena of $H_{00}$. The Hopf bifurcation in Fig. 1(a) is subcritical since stable behavior exists on only one side of the bifurcation point, while the bifurcation in Fig. 1(b) is supercritical because stable behavior is found on both sides of the bifurcation point. The particular diagrams shown in panels 1(c)–1(h) are chosen because of their implications for interpreting experimental data. Figures 1(e)–1(f) are bifurcation diagrams for $H_{01}$ with one set of unfolding coefficients for panels 1(e) and 1(d) and a second set for
TABLE II. Quantities used to construct bifurcation diagrams for the unfoldings of Table I. The Hopf bifurcation function is the power series expansion of $a_0$. If the function is negative (positive), the steady state is stable (unstable). A Hopf bifurcation occurs if the function is zero. Periodic orbits may exist even in the absence of a Hopf bifurcation. The orbit is stable if the stability function is negative. Note that this function is a constant for the $H_00$ and $H_00$ bifurcations, but that it depends on the parameters for the $H_0I$ bifurcation [the positive value of the stability function refers to the orbit resulting from use of the plus sign in Eq. (6)]. The coalescence of two limit cycles at a periodic orbit saddle-node bifurcation occurs when the periodic orbit stability function vanishes.

<table>
<thead>
<tr>
<th>Hopf bifurcation function</th>
<th>Region of existence</th>
<th>Stability function</th>
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<tbody>
<tr>
<td>$H_{00}$</td>
<td>$\frac{\partial a_0}{\partial a_1} \lambda_1$</td>
<td>$\frac{\partial a_0}{\partial a_1} \lambda_1 &lt; 0$</td>
</tr>
<tr>
<td>$H_{0I}$</td>
<td>$1 - 2 \alpha_1 \lambda_1^2 + \alpha_0 \lambda_2$</td>
<td>$\frac{1}{a_1} \left(1 - 2 \frac{\partial a_0}{\partial a_1} \lambda_1^2 + \frac{\partial a_0}{\partial a_1} \lambda_2 \right) &lt; 0$</td>
</tr>
<tr>
<td>$H_{10}$</td>
<td>$\frac{\partial a_0}{\partial a_1} \lambda_1 + \frac{\partial a_0}{\partial a_2} \lambda_2^2$</td>
<td>$a_2 \left[ -a_1 \pm \left(4a_0a_2\right)^{1/2} \right] &gt; 0$</td>
</tr>
</tbody>
</table>

panels 1(e) and 1(f). As the auxiliary bifurcation parameter is varied from panels 1(c) to 1(d), the two branches of stable orbits merge and then become isolated from the steady state branch. The resulting isolated branch of limit cycles is difficult to detect experimentally. In Figs. 1(e) and 1(f), as $\lambda_2$ is increased, a branch of unstable orbits connecting two Hopf points appears. Depending on the nature of the stable state not included in panels 1(e) and 1(f), the portion of the branch of steady states that becomes stable in panel 1(f) may not be detected without special search procedures. A numerical example for which this is true can be found in Ref. 40. Figures 1(g) and 1(h) are bifurcation diagrams for $H_{10}$. The notable feature in this case is the region of coexistence of a stable steady state and a stable periodic orbit shown in panel 1(g). This region of bistability disappears as the Hopf bifurcation changes from subcritical in Fig. 1(g) to supercritical in Fig. 1(h).

Verification of the correctness of the bifurcation diagrams of Fig. 1 follows from the formulas of Table II. Alternatively, a rapid appraisal of the validity of the bifurcation diagrams can be made using the exchange of stability principle. For the simple Hopf bifurcation of type $H_{00}$, the term “exchange of stability” arises from the fact that the limit cycle has the same stability as the steady state on the opposite side of the Hopf bifurcation point. An exchange of stability principle also holds at the periodic orbit saddle-node bifurcation in that the stability of the limit cycle changes at such points. Thus, given the direction of the branch of orbits at a Hopf bifurcation point and the stability of the steady state at one point, the assignment of stability for the entire diagram follows immediately by applying the exchange of stability principle.

For the simple Hopf bifurcation $H_{00}$, the steady state is stable, where $\lambda_1$ and $\partial a_0/\partial a_1$ are of opposite sign. The periodic orbit may or may not exist on the same side of $\lambda_1 = 0$ as does the stable steady state, depending on the sign of $a_1$. No behavior qualitatively different than that displayed in Figs. 1(a) and 1(b) occurs if the other sign of $\partial a_0/\partial a_1$ is used.

Because the universal unfolding of the $H_{0I}$ bifurcation [Eq. (1.2)] is an even function of $\lambda_1$, all possible bifurcation diagrams are symmetric about $\lambda_1 = 0$. The Hopf bifurcation function may have constant sign depending on the sign of $\lambda_2$. Since $\lambda_2$ takes on both positive and negative values in a full description of the unfolding, Hopf bifurcations are always present in one of the bifurcation diagrams and absent in the other. For example, if

$$\left(\frac{\partial^2 a_0}{\partial a_1^2}\right) \left(\frac{\partial a_0}{\partial a_1}\right) \lambda_2 > 0,$$

the Hopf bifurcation function does not change sign for $\lambda_2 > 0$. Such bifurcation diagrams can be seen in Figs. 1(d) and 1(e). The unfolding of $H_{01}$ exhibits two very different types of periodic orbit behavior as shown in Figs. 1(c), 1(d), and 1(f). If

$$a_1 \left(\frac{\partial^2 a_0}{\partial a_1^2}\right) > 0,$$

then the two Hopf bifurcations are connected by a branch of limit cycles. Otherwise, a distinct branch of orbits orig-
inates at each Hopf bifurcation. The two orbit branches are connected to the branch of steady states at the single degenerate Hopf point when \( \lambda_2 = 0 \), and a single branch of orbits, locally isolated from the branch of steady states, results upon further variation in the auxiliary parameter. Other bifurcation diagrams for this unfolding are obtained from those shown in Figs. 1(c)–1(f) by reversing the stability of all the solution branches.

The role of the distinguished parameter in defining the \( H_{01} \) bifurcation is made evident by examining Eq. (1.2) and the associated Hopf bifurcation function of Table II. If \( \lambda_1 \) is fixed and \( \lambda_2 \) is varied, the only difference between the \( H_{01} \) and \( H_{00} \) scenarios is that the Hopf bifurcation is offset from the origin of the parameter axis in the former case. The Hopf bifurcation curve near the degenerate point is the zero set in the \((\lambda_1, \lambda_2)\) plane of the Hopf bifurcation function. This relationship between \( \lambda_1 \) and \( \lambda_2 \) explains the presence of the quadratic fold in the bifurcation set about an \( H_{01} \) point.

Because of the \( \rho^r \) term in the unfolding of \( H_{10} \), it is easiest to analyze this bifurcation using Eq. (3) and substitute the series expansions for \( a_0 \) and \( a_1 \) afterwards. As in the above cases, Hopf bifurcation occurs when \( a_0 = 0 \). The Hopf bifurcation changes from subcritical to supercritical at an \( H_{10} \) bifurcation due to the change in sign of \( a_1 \). The nontrivial solutions \( \mathbf{v} = 0 \) satisfy the quadratic equation

\[
a_2(\rho^2) + a_1\rho^2 + a_0 = 0.
\]

When both roots of this equation are positive, two limit cycles exist in addition to the steady state. From the expression in Table II, we see that there are two periodic orbits if \( a_2 > 0 \), \( a_1 > 0 \), and \( 4a_0a_2 > a_1^2 \); one periodic orbit if \( a_2 < 0 \); and none in the remainder of the \((a_0, a_1)\) plane. The boundary between the region with two limit cycles and the region with none, a periodic orbit saddle-node bifurcation takes place. By an appropriate choice of the coefficients of Eq. (3), \( a_0 - \lambda_1 \) and \( a_1 - \lambda_2 \). Bifurcation diagrams for this parametrization of the unfolding with \( a_2 < 0 \) are given in Figs. 1(g) and 1(h). Other choices of the unfolding coefficients reverse the stability along the steady state branch and/or reverse the direction of the branch of orbits at the Hopf point.

More generally, at the level of approximation of Eq. (3), \( a_0 = 0 \) and \( a_1 = 0 \) are lines in the \((\lambda_1, \lambda_2)\) plane. Expressing \( a_0 \) and \( a_1 \) as linear functions of \( \lambda_1 \) and \( \lambda_2 \) can be thought of as a linear transformation from the \((a_0, a_1)\) plane to the \((\lambda_1, \lambda_2)\) plane, so the “quadrant” containing two periodic orbits can still be identified. Recalling that \( a_0 \) determines the stability of the steady state and \( a_1 \) determines the stability of the periodic orbit, this quadrant is identified by the nature of the steady state (stable or unstable) in its interior and by the type of Hopf bifurcation (subcritical or supercritical) on its boundary. In this way, we know whether the periodic orbit saddle-node bifurcation occurs at a parameter value greater or less than that at the Hopf point.

Since there is no distinguished parameter, both \((r, \lambda_1)\) and \((r, \lambda_2)\) bifurcation diagrams are of interest. After selecting the primary bifurcation parameter and choosing a value for the auxiliary parameter, the value of the primary parameter at the Hopf bifurcation point is found from \( a_0 = 0 \). The pair of parameters is then substituted into the expression for \( a_1 \) to determine the nature of the Hopf bifurcation, and from this, it is known if the branch of limit cycles exhibits a periodic orbit saddle-node bifurcation.

### III. NUMERICAL METHODS

Bifurcation analysis proceeds in two steps—detection, followed by identification. For the degenerate Hopf bifurcation \( H_{01} \) (with respect to \( H_{10} \)), detection involves verifying that hypothesis (H2) [with respect to hypothesis (H3)] does not hold. Identification requires confirming that hypothesis (H3) [with respect to hypothesis (H2)] as well as the additional conditions given in the previous section are satisfied and then calculating the coefficients of the universal unfolding. Hypothesis (H1) along with the verification of either hypothesis (H2) or hypothesis (H3) constitute the defining conditions of the degenerate bifurcation.

First, a Hopf bifurcation must be located. This is done with the numerical bifurcation analysis package AUTO. After a codimension one Hopf bifurcation point is found, AUTO is used to generate a sequence of points on a relatively coarse mesh (e.g., 20 points per logarithmic unit) along a two-parameter Hopf bifurcation curve. Next, the quantities \( a_1, \partial a_0/\partial \lambda_1 \), and \( \partial a_0/\partial \lambda_2 \) are evaluated at each of these points using a collection of subroutines developed by Hassard and co-workers. These subroutines compute the coefficients \( a_i \) of Eq. (3) and the derivatives of the coefficients with respect to the bifurcation parameters, so both detection and identification are accomplished using them. Whenever a zero crossing of one of these coefficients occurs, a neighborhood of a degenerate bifurcation has been detected.

After a zero crossing has been bracketed, the software of Hassard et al. is used in an attempt to locate accurately the degenerate point by applying Newton–Raphson iteration to the augmented system obtained by appending the equations for the defining conditions to Eq. (2) for the steady state. If the point on the original coarse mesh that is nearest the zero crossing is used as the initial guess, convergence to the degenerate point is usually achieved. If necessary, a finer mesh is generated with AUTO and the process is repeated. Convergence is signaled if the Euclidean norm of either the vector of defining conditions or its Newton–Raphson update is below a user-specified threshold (10⁻¹⁰ by default). When convergence is achieved, the requisite unfolding coefficients are computed. Sometimes it is not possible to obtain convergence, even with an initial guess for which the defining conditions are as small as 10⁻⁸. In such cases, the unfolding coefficients are computed in a neighborhood of the zero crossing. This does not cause any difficulties in the interpretation of the results so long as the unfolding coefficients do not change sign in the chosen neighborhood.

To explore the dynamical behavior that results from a particular degeneracy (or combination of degeneracies), branches of periodic orbits can be calculated using AUTO.
For the default definition of pseudoarc length and the unscaled vector fields derived from the reaction mechanisms, the change in bifurcation parameter per step is exceedingly small, causing such calculations to be prohibitively slow. If the species’ concentrations are put on a logarithmic scale, this difficulty is overcome. This is a brute force method of obtaining variables that are all of similar magnitude, but it has the virtue of being problem independent. An improved method of calculating the Floquet multipliers for the periodic orbits was substituted for that found in the standard version of AUTO.

The strategy outlined above retains the feature of computational economy that we stressed in the preceding paper because detection and identification of the degeneracy only require information about the bifurcating steady state. For example, a typical degenerate Hopf bifurcation can be identified in about one-half the time required to calculate a branch of orbits such as that of Fig. 8(a); branches such as those of Figs. 7 and 8(d) take ten to 100 times as long to compute. Careful consideration of the unfoldings serves to pinpoint regions of parameter space that possess distinctive dynamics; therefore, the more resource intensive aspects of the analysis can be limited to the features of greatest interest.

IV. DEGENERATE HOPF BIFURCATIONS IN A CHEMICAL REACTION MECHANISM

A multiparameter Hopf bifurcation analysis of mechanism MO of the chlorite-iodide reaction will illustrate how the theory and methods described in Secs. II and III are applied to an actual chemical reaction mechanism. The reactions and associated rate laws of mechanism MO can be found in Ref. 4. In a typical experiment involving this reaction, there are four parameters—flow rate \( k_0 \), acidity \([\text{H}^+]\), and feed stream concentrations of chlorite ion and iodide ion \([\text{ClO}_2^-]_0\) and \([\text{I}^-]_0\). The mechanism includes seven chemical species \(\text{HClO}_3, \text{ClO}_2^-, \text{HOCl}, \text{HIO}_3, \text{HIO}_2, \text{I}_2\) and \(\text{I}^-\), with \(\text{HClO}_2\) and \(\text{ClO}_2^-\) assumed to be in rapid equilibrium.

The flow rate \( k_0 \) is taken as one of the parameters in our calculations since it is commonly used as an experimental bifurcation parameter. Both batch kinetic investigations and CSTR studies of the redox reactions of the oxyhalogens typically show a pronounced dependence on the hydrogen ion concentration. By choosing \([\text{H}^+]\) as the second parameter in two-parameter bifurcation sets, we can determine the behavior predicted by the model over a wide range of acidities. Major improvements in the mechanisms of oxyhalogen-based oscillating reactions should accrue if the sensitivity of these reactions to \([\text{H}^+]\) is exploited. Numerical bifurcation analysis can be used to rapidly examine proposed mechanisms and to suggest specific regions of parameter space on which further experimental attention should be focused.

Before proceeding to the two-parameter analysis, we give an example of unfolding a generic Hopf bifurcation. A representative curve of steady states as a function of flow rate is shown in Fig. 2(a). For the chosen parameter values, a Hopf bifurcation is found at \( k_0 = 1.34 \times 10^{-3} \text{s}^{-1} \). While the direction of the branch of periodic orbits at the Hopf point is unknown until the universal unfolding is computed, we can conclude that if the initial direction is towards lower flow rates, then one or more bifurcations remain undetected. This follows from the fact that there is no stable steady state in the flow rate interval between the
Hopf bifurcation and the saddle-node bifurcation labeled SN1.

Since only one parameter is being varied, the relevant equation for the unfolding is Eq. (1.1) with \( k_0 \) taking the place of \( \lambda_1 \). We find that \( \partial a_0 / \partial k_0 = 110 \) and \( a_1 = 0.20 \), so the equation becomes

\[
\dot{r} = -r(110k_0 + 0.2r^2).
\] 

Recall that in writing an equation for a universal unfolding, the origin of parameter space is shifted to the bifurcation point, so that \( k_0 < 0 \) is understood to mean that \( k_0 < k_0^* \). A bifurcation diagram valid in a neighborhood of the Hopf point can be obtained by applying the results of Sec. II to Eq. (7). The Hopf bifurcation function is \( 110k_0 \), so the steady state is stable for flow rates to the left of the Hopf bifurcation point. Although this was already known from Fig. 2(a), it is a useful check of Eq. (7). Since \( \partial a_0 / \partial k_0 \) and \( a_1 \) have the same sign, the branch of orbits is directed initially from the Hopf point towards lower flow rates. From Table II, we find that the orbit is unstable because \( a_1 > 0 \). As an additional check of consistency, note that the periodic orbit is predicted to exist in the same flow rate range as the stable steady state. Therefore, the orbit must be unstable, since a stable steady state cannot be enclosed by a stable orbit without an intervening unstable limit set (e.g., an unstable limit cycle). A closeup of the bifurcation diagram as computed by AUTO is displayed in Fig. 2(b). The behavior found by direct calculation is exactly as predicted by Eq. (7).

The universal unfolding of the simple Hopf bifurcation predicts that the amplitude of the limit cycle depends on the square root of the distance of the parameter from the bifurcation point. The deviation from this prediction evident in Fig. 2(b) is a graphic reminder of the local nature of an unfolding. In this case, the neighborhood in which the unfolding can be applied quantitatively is rather small. If it is necessary to indicate the source of a bifurcation diagram, one deduced from an unfolding will be called local, while one computed for the entire set of equations over a broad range of the parameter will be called global. The convention regarding the use of stable and unstable introduced in the discussion of Fig. 2 is made explicit here. If the system returns to its initial state after sufficiently small perturbations, then it is stable; otherwise, it is unstable. Although many types of asymptotic behavior are thus lumped together under the heading unstable, they share the common feature of being experimentally unobservable. As the number of variables (chemical species) increases, it is likely that an unstable object has both stable and unstable eigenvectors that describe its response to particular perturbations. Such an object is more properly called a saddle. For example, the periodic orbit of Fig. 2(b) has four stable directions and one unstable direction. Owing to the noise that is inevitably present in an actual experiment, the presence of even one unstable direction renders a limit set unobservable, so we reserve the use of the term saddle for situations in which it is necessary to stress the existence of both stable and unstable eigenvectors.

The discussion of the codimension two Hopf bifurcations is organized as follows: universal unfoldings will be presented for \( H_{01} \) bifurcations, first for those having \( k_0 \) as the distinguished parameter and then for those with \([H^+]\) as the distinguished parameter. Then the unfoldings of the \( H_{10} \) bifurcations will be given. Next, the global periodic orbit structure will be discussed. Keeping in mind the constraints imposed by the local character of the analysis, universal unfoldings are patched together to gain insight into the global dynamics. This section is concluded by considering which of the features revealed by the analysis are most amenable to experimental test.

### A. Identification of codimension two Hopf points

With \([\text{ClO}_2^-]\)\(_p\)(\([I^-]\)_b) fixed at \(5 \times 10^{-4} \text{ and } 1 \times 10^{-3} \text{ M}\), the two-parameter steady state bifurcation set shown in Fig. 3(a) is obtained. The points labeled A-I on the curve of Hopf bifurcations are codimension two points. Inspection of the two-parameter Hopf bifurcation curve for quadratic segments is a useful preliminary step in the detection of \( H_{01} \) points. The identity of the distinguished parameter is an immediate consequence of the orientation of such a segment with respect to the parameter axes. Quadratic folds can be readily seen at points D and H. Upon magnifying the curve in the vicinity of points A and B and points F and G [Figs. 3(b) and 3(c), respectively], the folds are revealed at these points as well. Figure 3(d) serves to locate point I with respect to the Takens-Bogdanov point TB3 that results from the interaction of the Hopf and saddle-node curves. Points A, B, and H are \( H_{01} \) bifurcations with flow rate as the distinguished parameter; points D, F, and G are \( H_{01} \) bifurcations with \([H^+]\) as the distinguished parameter; and points C, E, and I and \( H_{10} \) bifurcations. The latter three points divide the Hopf bifurcation curve into four segments according to the stability of the limit cycle resulting from the bifurcation. \( a_1 > 0 \) near TB1, so the limit cycle is unstable from TB1 to C and from E to I, while it is stable from C to E and from I to TB2.

The coordinates of points A-I and their universal unfoldings are found in Table III. Upon further consideration of the discussion of Sec. II, we see that in order to extract information regarding existence and stability of periodic orbits near an \( H_{01} \) bifurcation, only the signs of the unfolding coefficients are needed. On the other hand, analysis of an \( H_{10} \) bifurcation requires the values of the coefficients, and information about the curvature of the Hopf bifurcation set can be derived from the magnitudes of the coefficients in the case of the \( H_{01} \) degeneracy, so values for all the unfolding coefficients are given in the table.

From Table III, we see that the unfolding at A is essentially the same as that of Figs. 1(e) and 1(f) with the only difference being the sign of \( \partial a_0 / \partial k_2 \) (here \( \lambda_2 = [H^+] \)). This coefficient is multiplied by \( \lambda_2 \) in the unfolding, so the effect of the reversal in sign is a concommitant reversal in the \( \lambda_2 \) axis. Consequently, the bifurcation diagram of Fig. 1(f) in which \( \lambda_2 > 0 \) applies to \([H^+]_b > 0.497 \text{ M}\). The branch of connecting orbits and associated steady state behavior can be seen in Fig. 4(a). It is clear from Fig. 3(b)
FIG. 3. Bifurcation sets in the \((k_0, [H^+])\) plane for mechanism \(M_1\). Fixed parameters have the values \(([\text{ClO}_2], [\text{I}^-]) = (5 \times 10^{-4}, \text{and } 1 \times 10^{-3} \text{ M})\). Solid lines denote saddle-node curves and dotted lines denote Hopf bifurcation curves. The Hopf curve originates at the Takens-Bogdanov bifurcation points indicated by \(A-I\). The coefficient of the lowest-order nonlinear term of the universal unfolding [Eq. (3)] vanishes at points \(C, E,\) and \(F\), while quadratic folds occur at points \(A, B, D, F, G,\) and \(H\). The boxes in (a) are not drawn to scale. The features enclosed in these boxes are redrawn on expanded scales in (b), (c), and (d).

that a bifurcation diagram for \([H^+] < [H^+]_A\) has no Hopf points near \(A\).

By factoring \(-1\) out of the unfolding at \(B\), we see that nearby bifurcation diagrams are the same as those of Figs. 1(c) and 1(d) with stabilities reversed due to the minus sign. The local bifurcation behavior for \([H^+] < [H^+]_B\) is shown in Fig. 4(b). For \([H^+] > [H^+]_B\), we expect the branch of periodic orbits to be locally isolated near \(B\). The lifting of the branch of orbits from the branch of steady states can be seen in Fig. 4(c). The large separation between the Hopf bifurcation points in Figs. 4(a) and 4(b) even for \([H^+]\) very near to the degeneracy is expected in view of the small curvature of the Hopf bifurcation set [evident in Fig. 3(a)] near both \(A\) and \(B\). The small curvature follows immediately from the unfolding coefficients multiplying \(k_0^2\) and \([H^+]\).

When \(-1\) is factored out of the unfolding at \(H\), we see that the bifurcation diagrams are obtained from those of Figs. 1(c) and 1(d) by reversing stability to account for the minus sign and by reversing the orientation of the \([H^+]\)
TABLE III. Logarithms of the coordinates in the \((k_c, [H^+])\) plane of the codimension two Hopf bifurcations of mechanism MO displayed in Fig. 3(a) and the associated universal unfoldings.

<table>
<thead>
<tr>
<th>Coordinates</th>
<th>Unfolding</th>
</tr>
</thead>
<tbody>
<tr>
<td>((-0.82, -0.30))</td>
<td>(r = r(2.6k_c^2 - 1.4[H^+] + 2.4r^2))</td>
</tr>
<tr>
<td>((1.54, -0.28))</td>
<td>(r = r(-20k_c^2 - 0.9[H^+] - 1.4r^2))</td>
</tr>
<tr>
<td>((-1.94, -0.30))</td>
<td>(r = r(2.9k_0 - 0.81[H^+] + (170k_0 - 9.3[H^+])r^2 + 2.3r^4))</td>
</tr>
<tr>
<td>((-3.19, -0.96))</td>
<td>(r = r(450k_0 - 12[H^+]^2 - 1.4r^2))</td>
</tr>
<tr>
<td>((-3.13, -1.22))</td>
<td>(r = r(380k_0 + 2.0[H^+] + (6400k_0 - 3.7[H^+])r^2 - 8.2r^4))</td>
</tr>
<tr>
<td>((-2.87, -1.99))</td>
<td>(r = r(110k_0 + 180[H^+]^2 + 0.21r^2))</td>
</tr>
<tr>
<td>((-2.92, -2.87))</td>
<td>(r = r(21k_0 - 650[H^+]^2 + 0.12r^2))</td>
</tr>
<tr>
<td>((-2.75, -3.60))</td>
<td>(r = r(-1700k_0 + 9.0[H^+] + 0.0057r^2))</td>
</tr>
<tr>
<td>((-2.49, -3.41))</td>
<td>(r = r(-2.2k_0 + 15[H^+] - (16k_0 + 57[H^+])r^2 - 0.075r^4))</td>
</tr>
</tbody>
</table>

axis to account for the sign of the derivative of \(a_0\) with respect to this parameter. Thus, there are two branches of unstable periodic orbits for \([H^+] > [H^+]_{ph}\) and a locally isolated branch of unstable orbits if \([H^+] < [H^+]_{ph}\).

The unfolding of the degenerate bifurcation at \(D\) implies that for \(k_0 < k_0, D\) there are no periodic orbits, and that for \(k_0 > k_0, D\) the two Hopf points are connected by a branch of stable orbits. Points \(F\) and \(G\) are analogous to \(A\) and \(B\), respectively, with \([H^+]\) replacing \(k_0\) as the distinguished parameter and with the orientation of the auxiliary parameter axis reversed.

At point \(C\), \(a_2 > 0\), implying that a curve of periodic orbit saddle-node bifurcations is found at values of \((k_0, [H^+])\) such that \(a_0 > 0\) and \(a_1 < 0\). From the second of these conditions, we conclude that if the Hopf bifurcation is supercritical, then the branch of limit cycles possesses a saddle-node bifurcation. Taking the signs of \(\partial a_0/\partial k_0\) and \(\partial a_0/\partial [H^+]\) into account, the first condition leads to the

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**FIG. 4.** Bifurcation diagrams near points \(A\) and \(B\) of Fig. 3(b). \(k_0\) is the distinguished parameter with \([H^+] = 0.51\) M in (a) and (b) and \([H^+] = 0.53\) M in (c). The number of Hopf bifurcation points decreases by two and the branch of unstable orbits becomes locally isolated as \([H^+]\) increases beyond the maximum in the Hopf bifurcation curve at \([H^+] \approx 0.52\) M.
FIG. 5. \{log([I^-]), k_0\} and \{log([I^-]), [H^+]\} bifurcation diagrams in a neighborhood of the $H_1$ point $E$. At $E$, $k_0=7.47\times10^{-4}$ s$^{-1}$ and $[H^+]=6.07 \times10^{-2}$ M. The values of the auxiliary parameter are $[H^+]=6.0\times10^{-2}$ M in (a), $[H^+]=6.1\times10^{-2}$ M in (b), $k_0=7.4\times10^{-4}$ s$^{-1}$ in (c), and $k_0=7.5\times10^{-4}$ s$^{-1}$ in (d).

conclusion that the turning point on the branch of orbits is found to the right of the Hopf bifurcation point when $k_0$ is the primary parameter and to the left of the Hopf bifurcation point when $[H^+]$ is the primary parameter. It turns out that these predictions are difficult to confirm. The occurrence of a cusp point on the curve of periodic orbit saddle-node bifurcations very close to $E$ causes the neighborhood in which this local analysis applies to be extremely small.

There are no complications of this type near $E$. Because $a_2<0$ in this case, the subcritical segment of the Hopf bifurcation curve is tangent to the curve of periodic orbit saddle-node bifurcations at $E$. The subsidiary bifurcations along the branch of limit cycles occur in the region where the steady state is stable, leading to the coexistence of a stable steady state and a stable periodic orbit. Recollecting that Hopf bifurcations between points $E$ and $I$ are subcritical, we expect bifurcation diagrams with $k_0$ as the free parameter to show periodic orbit saddle-node bifurcations at flow rates to the left of the Hopf bifurcation for $[H^+]<[H^+]_E$. If $[H^+]$ is the primary parameter, then $k_0$ must be greater than $k_{0,E}$ to observe multistability, which again exists to the left of the Hopf bifurcation. Calculated bifurcation diagrams confirming this scenario are found in Fig. 5.

The sign of $a_2$ at point $I$ is the same as at point $E$, so periodic orbit saddle-node bifurcations are anticipated in the region associated with a stable steady state and subcritical Hopf bifurcation. Because $\partial a_2/\partial k_0<0$ and $\partial a_2/\partial [H^+]>0$, this region is below and to the left of $I$ in the $(k_0,[H^+])$ plane.

B. Predicting global dynamics

In the preceding subsection, we demonstrated that local bifurcation information could be derived reliably from the universal unfolding at a degenerate Hopf point. However, as in the case of point $C$, the region in which the information is valid may be too small to be resolved experimentally. Since our principle objective is the proposal of definitive experimental tests of a mechanism, we now turn to the situation in which universal unfoldings are used to guide speculation about dynamical phenomena that are robust in the sense that they persist over easily measurable regions of parameter space. By taking additional features of the bifurcation structure into account, one can extend
with the middle Hopf point migrating from high to low flow rates as the acidity increases. Upon interchanging the axes of Fig. 3(b), one is reminded of the familiar S-shaped hysteresis curve. Note that the sign of $\delta a_0 / \partial k_0$ at $A$ is opposite that at $B$, as it must be given the change in curvature at the two points. It is reasonable to anticipate that variation of a third parameter will lead to a Hopf bifurcation curve with a cubic inflection point. The Hopf bifurcation (denoted by $H_{B2}$) occurring at this type of inflection point has codimension three with the universal unfolding (up to reversal of stability) given by $r = r_0 (r^2 - \lambda_1^2 + \lambda_2 + \lambda_3 \lambda_2)$. Given $\lambda_2$ and $\lambda_3$, the presence of either one or three Hopf points in the $(r, \lambda_1)$ bifurcation diagram is deduced from the unfolding. $A$ and $B$ disappear from Hopf bifurcation curves at nearby values of $[\text{ClO}_2^-]_0$ and $[\text{I}^-]_0$, as $[\text{ClO}_2^-]_0$ is decreased or as $[\text{I}^-]_0$ is increased, supporting the existence of such a codimension three point.

The fate of a locally isolated branch of orbits is another example of the type of global information we seek. We expect the region of parameter space in which periodic behavior is found to be finite, so all branches of orbits must terminate at a bifurcation point. In one-parameter problems, there are only three ways in which an orbit can disappear without giving rise to other asymptotic solutions of the rate equations. In addition to Hopf bifurcation and periodic orbit saddle-node bifurcation, it may happen that an orbit collides with a saddle point, producing a homoclinic bifurcation. If all the branches of orbits are not terminated in the local analysis, then the simplest global bifurcation diagram is obtained by completing the diagram with some combination of the three bifurcations listed above. In this context, simplest refers to the absence of any new asymptotic solutions in the global bifurcation diagram. If a locally isolated branch of orbits remains separated from the steady state branch for all parameter values, stable dynamics on this closed loop (also known as an isola) of limit cycles may be overlooked. Finding such dynamics by direct simulation alone requires either a fortuitous choice of parameter paths or a more exhaustive search of parameter space than is typically undertaken.

In the case of the branch of orbits that becomes isolated due to the degenerate Hopf point $B$, note that $B$ is inside the cusp-shaped region of steady state multiplicity and that a Hopf bifurcation at high flow rates still exists for $[\text{H}^+] > [\text{H}^+]_B$. None of the above means of terminating the branch of orbits can be ruled out; in particular, there is no reason to favor an explanation leading to a closed loop of limit cycles. In fact, given the link between $A$ and $B$, it is more likely that the branch of orbits remains anchored to the steady state branch at the high flow rate Hopf point. Continuation of the branch of orbits shown in Fig. 4(c) to higher flow rates proves this latter conjecture correct, as can be seen in Fig. 6(b).

The location of $H$ allows us to make a firmer case for the existence of an isola of periodic orbits. In this region of parameter space, the only Hopf bifurcations occur near $H$ and the interval of steady state bistability is small when $k_0$ is the distinguished parameter. For these reasons, we anticipate that if $[\text{H}^+] < [\text{H}^+]_B$ then the branch of orbits...
changes direction and stability on the left at a periodic orbit saddle-node bifurcation. The conjectured bifurcation diagram is still incomplete; two limit cycle branches (one stable, one unstable) remain detached. The only suggestion of nearby homoclinic behavior is the Takens–Bogdanov point TB₂. Since Hopf bifurcations between I and TB₂ are supercritical, the curve of homoclinic orbits emanating from TB₂ must involve a stable limit cycle. We tentatively reject the disappearance of the unstable limit cycle via a homoclinic bifurcation, as this would require a rather complicated global bifurcation structure to exist. On this basis, bifurcation diagrams are computed for \([H^+] = 2.4 \times 10^{-4}\) and \(2.6 \times 10^{-4}\) M. The existence of an isolated closed loop of orbits is confirmed; its evolution can be seen in Fig. 7.

When the steady state is unique throughout the region of interest, all bifurcations must be local and stronger conclusions can be drawn as a result. This is illustrated by considering bifurcation diagrams with \([H^+]\) as the distinguished parameter in the region \(k_c < k_{oc} \). The steady state is stable when \(k_0 < k_{0,D}\). For \(k_{0,D} < k_0 < k_{0,F}\), there are two Hopf bifurcations. Because no other degenerate Hopf bifurcation has been encountered, the local information valid in a neighborhood of \(D\) can be extended to this entire interval of \(k_0\). The branch of connecting orbits is illustrated in Fig. 8(a) for \(k_0 = 7.0 \times 10^{-4}\) s⁻¹. As \(k_0\) is increased beyond \(k_{0,B}\), the Hopf bifurcation at lower \([H^+]\) becomes subcritical. The branch of orbits continues to connect the two Hopf points, but there is now a periodic orbit saddle-node bifurcation on the branch. This behavior can be seen in Fig. 8(b), where \(k_0 = 8.0 \times 10^{-4}\) s⁻¹. A branch of orbits becomes attached to the branch of steady states at \(k_{0,G}\). Between \(F\) and \(G\), there are four Hopf bifurcations on the steady state branch. Upon continued increase of \(k_0\), the two Hopf points at intermediate values of \([H^+]\) merge and the branch of unstable connecting orbits disappears at \(k_0 - k_{0,F}\). Points \(F\) and \(G\) interact in the same way as do points \(A\) and \(B\). This is illustrated in Fig. 8(c) by the dual role of the Hopf point at \(\log([H^+]) = -2.3\). The branch of orbits for \(k_0 = 1.4 \times 10^{-3}\) s⁻¹ > \(k_{0,F}\) is shown in Fig. 8(d). Observe that there is a remarkable increase in the interval of \([H^+]\) for which stable periodic orbits are found between Figs. 8(b) and 8(c). One explanation is that a closed loop involving the isolated branch near \(G\) merged with a branch of orbits typified by that of Fig. 8(b) to form a single branch extending to low \([H^+]\). This requires two codimension two bifurcations of periodic orbits—one at the origin of the closed loop and one at the merging of the two previously independent branches of limit cycles. The second of these is a transcritical bifurcation and it arises naturally in the unfolding of the codimension three Hopf bifurcation (denoted by \(H_{11}\)) satisfying \(a_0 - \partial a_0/\partial [H^+] = a_1 = 0\). Although no attempt was made to locate such a degeneracy, the existence of two branches of periodic orbits as described above is demonstrated clearly by Fig. 9.

C. Suggested experiments

The list of codimension two steady state bifurcations of mechanism \(M0\) consists of the degenerate Hopf bifurcations of Table III, the steady state cusp, and the two
FIG. 8. Bifurcation diagrams with respect to \([H^+]\) illustrating the interaction of points \(D, E, F,\) and \(G\) of Fig. 3(a). \(k_0\) has the values \(7.0 \times 10^{-4}\), 
\(8.0 \times 10^{-4}\), \(1.3 \times 10^{-3}\), and \(1.4 \times 10^{-3} \text{ s}^{-1}\) in (a)-(d), respectively.

Takens–Bogdanov points for \(([\text{ClO}_2^-]_0 / [I^-]_0) = (5 \times 10^{-4}\) and \(1 \times 10^{-3} \text{ M}\). Substantial hints about the periodic orbit bifurcation structure have been gained in the process of identifying the codimension two Hopf points. The power of a numerical bifurcation analysis of a chemical reaction mechanism is manifested by the generation of a set of experiments that will test the model on the basis of the dynamical features found in the course of the calculations. We now derive such a set of experiments from the observations of the preceding subsections.

A large-scale feature evident without calculating unfoldings of the codimension two Hopf points is the region at lower flow rates roughly bounded by the Hopf bifurcation curve on the left and the steady state saddle-node curve on the right. The unique steady state is unstable in this region, so the asymptotic dynamics must be time dependent. The prediction of oscillatory behavior at the relatively low values of the \([\text{ClO}_2^-]_0 / [I^-]_0\) ratio and \([H^+]\) reported here is certainly of interest. We have experimentally verified the existence of oscillations at \([H^+] = 1.0 \times 10^{-3} \text{ M},\) albeit at a \([\text{ClO}_2^-]_0 / [I^-]_0\) ratio of 1/3.5 rather than 1/2.4.

Although the calculations presented here do not indicate the extent of the region in which the closed loop of

FIG. 9. Bifurcation diagram with respect to \([H^+]\) at \(k_0 = 1.17 \times 10^{-3} \text{ s}^{-1}\) illustrating the existence of an isolated branch of periodic orbits.
limit cycles resulting from point \( H \) persists, the experiments required to find the isola would not be difficult if the region is sufficiently sizeable. Beginning with \([H^+]\) as the primary parameter, stable oscillations could be tracked as the acidity is lowered until the oscillations disappear. After returning to the oscillatory branch by increasing \([H^+]\), the flow rate would then be varied at fixed \([H^+]\) to discover the nature of the bifurcations leading to the loss of the limit cycle. Two experiments would be required—one as flow rate is increased and one as it is decreased. If the system can be perturbed from the limit cycle to the coexistent steady state and if varying the flow rate in both directions along the branch of steady states does not cause a transition back to the limit cycle, the existence of a closed loop of orbits would be conclusively demonstrated. Recalling that an isola is relatively difficult to find using other numerical techniques, it is likely that this experiment would not even be proposed on the basis of a more traditional mechanistic analysis.

Of the three \( H_{10} \) points, \( E \) and \( I \) imply the existence of bistability between a steady state and a periodic orbit. Of these two, \( E \) is the better candidate for experimental investigation, since the region near \( I \) is complicated by \( T_{B_2} \). Figure 8 shows that \( E \) exerts an influence over a substantial region of parameter space in that a periodic orbit saddle-node bifurcation appears in all the bifurcation diagrams with \( k_0 > k_{0,E} \). Because this bifurcation has codimension one, it does not require a distinguished parameter. Therefore, the sequence of bifurcation diagrams in Fig. 8 provides evidence of bistability between a steady state and a limit cycle when \( k_0 \) is the primary parameter as well. Figure 8 also supports our assertion that \([H^+]\) has a dramatic effect on the system. While particular aspects of this series of bifurcation diagrams may prove to be beyond experimental resolution, the general utility of \([H^+]\) as the primary bifurcation parameter at low flow rates is worth noting.

There are many other features which are surely difficult to probe experimentally. For example, the structure near points \( A \) and \( B \) is responsible for a large shift in the location of the Hopf bifurcation as one increases the flow rate from low to high values, but this shift occurs for a change of only 0.02 M in \([H^+]\). This is one instance that calls for more computations; Hopf bifurcation curves at other chlorite ion and iodide ion feed stream concentrations might reveal conditions under which these folds are more pronounced.

V. COMPARISON OF MECHANISMS \( M_0, M_1, \) AND \( M_3 \)

After identifying regions of parameter space possessing distinctive time-dependent asymptotic behavior for a given mechanism, the logical extension of the method is a comparison of these regions for alternative mechanisms. If the differences in mechanism are relatively small, such a comparison may give an idea of the sensitivity to changes in a particular rate constant or rate expression. We have selected three mechanisms of the chlorite–iodide reaction for such a comparative study. Reference 4 contains the description of mechanisms \( M_0 \) and \( M_1 \). \( M_3 \) is obtained from \( M_0 \) by replacing \( R_{1,M0} \) by \( R_{1,M3} \) and \( R_{4,M0} \) by \( R_{4,M3} \), where

\[
R_{1,M3} = \frac{k_{1,M3}K_{a,M3}[H^+]}{2([H^+]+K_{a,M3})}[\text{Cl}(III)][I^-],
\]

\[
k_{1,M3} = 9.2 \times 10^2 \text{ M}^{-2} \text{s}^{-1},
\]

\[
K_{a,M3} = 0.01 \text{ M}
\]

and

\[
R_{4,M3} = \frac{k_{4,M3}K_{a,M3}[H^+]}{2K_a([H^+]+K_{a,M3})}[\text{Cl}(III)][\text{HOI}],
\]

\[
k_{4,M3} = 5.1 \times 10^{-3} \text{ s}^{-1},
\]

\[
K_a = 3.13 \times 10^{-13} \text{ M}^2.
\]

\( M_1 \) and \( M_3 \) are derived from \( M_0 \) by changing the rate expression for the reaction between \( \text{ClO}_2^- \) and \( \Gamma^- \). In \( M_0 \), both \( \text{ClO}_2^- \) and \( \text{HClO}_2 \) are assumed to be equally reactive towards iodide. In the development of \( M_0 \), it was found that this assumption led to a desired shortening of the period of oscillation, but the supposed reactivity of \( \text{ClO}_2^- \) is in disagreement with the batch kinetic experiments of Kern and Kim. A rate expression consistent with the earlier batch results is used in \( M_3 \). \( M_1 \) utilizes the rate law reported by Song et al. In this study, the initial stage of the chlorite–iodide reaction was reinvestigated at higher acidity, and a pathway second order in \([H^+]\) was discovered. Since the hydrogen ion concentration changes only by changing the composition of the feed streams, the actual rate constants, equilibrium constants, and \([H^+]\) can be combined into apparent rate constants. The three apparent
rate constants for the reaction of ClO₃⁻ with I⁻ are displayed as a function of hydrogen ion concentration in Fig. 10. \(k_{\text{app,1,M0}}\) increases linearly. \(k_{\text{app,1,M1}}\) plateaus briefly at intermediate \([H^+]\) and resumes increasing as the second-order pathway becomes predominant. \(k_{\text{app,1,M3}}\) is essentially constant for \([H^+] > 10k_{\text{app,M3}}\), reflecting the fact that nearly all Cl(III) is in the protonated, reactive form at high acidities. The rate expression for the reaction between chlorite and hypohioud acid is also changed. This amounts to using the same value for the iodine hydrolysis equilibrium constant throughout the mechanism in the case of M3. In the case of M1, an additional change is made to account for the new value of the acid dissociation constant of HClO₃ derived in the course of the kinetic analysis. These revisions change the magnitudes of the apparent rate constants, but do not alter the form of their dependence on \([H^+]\). The apparent rate constants all approach a constant value as the hydrogen ion concentration is increased.

Steady state saddle-node and Hopf bifurcation curves of M1 for the constraints of Sec. IV are shown in Fig. 11. The unfoldings of the degenerate Hopf bifurcations are listed in Table IV. The corresponding data for M3 are given in Fig. 12 and Table V. The first impression upon comparing Figs. 3(a), 11(a), and 12 is that the diagrams are remarkably similar in appearance. The same type and number of steady state bifurcation curves are present in each of the three diagrams. MO and M3 even have the same ordering of degenerate points along the Hopf bifurcation curve. An important common feature is the rather large area at lower flow rates in which the unique steady state is unstable. In all three cases, supercritical Hopf bifurcations exist at high acidities in the region of steady state multiplicity. This implies that there is a bistability between the high flow rate branch of steady states and a limit cycle. Such behavior was found in the original experimental investigation of this system, but it has not been reported for previous calculations. The parameters of the experiment differ from those of our calculation, but the result is encouraging nonetheless. The isola of periodic orbits found near point H of mechanism M0 is certain to exist for M1 (the minimum in the Hopf curve is below the steady state cusp point) and assumed to exist for M3 (on the basis of the similarity of the three bifurcation sets).

Yet, in spite of this first impression, there are poten-
FIG. 12. Bifurcation sets in the \((k_r[H^+])\) plane for mechanism M3 for the same value of \((\text{[ClO}_3^-]_{p0}[\Gamma^-]_{p0})\) as in Fig. 3.

Table V. Logarithms of the coordinates in the \((k_r[H^+])\) plane of the codimension two Hopf bifurcations of mechanism M3 displayed in Fig. 12 and the associated universal unfoldings.

<table>
<thead>
<tr>
<th>Coordinates</th>
<th>Unfolding</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ((-0.84, -0.43))</td>
<td>(r = r(2.4k_r^2 - 1.9[H^+] + 2.9r^2))</td>
</tr>
<tr>
<td>B ((1.44, 0.12))</td>
<td>(r = r(14k_r^2 - 1.6[H^+] + 3.6r^2))</td>
</tr>
<tr>
<td>C ((-2.01, -0.45))</td>
<td>(r = r(4.3k_r - 1.3[H^+] + (650k_r - 33[H^+])r^2 + 49r^4))</td>
</tr>
<tr>
<td>D ((-3.06, -0.97))</td>
<td>(r = r(360k_r - 15[H^+])^2 - 1.6r^2)</td>
</tr>
<tr>
<td>E ((-3.00, -1.20))</td>
<td>(r = r(320k_r + 2.1[H^+] + (500k_r - 7.5[H^+])r^2 - 9.9r^4))</td>
</tr>
<tr>
<td>F ((-2.75, -1.98))</td>
<td>(r = r(97k_r + 200[H^+])^2 + 0.25r^2)</td>
</tr>
<tr>
<td>G ((-2.79, -2.85))</td>
<td>(r = r(18k_r - 730[H^+])^2 + 0.15r^2)</td>
</tr>
<tr>
<td>H ((-2.63, -3.53))</td>
<td>(r = r(-1300k_r + 10[H^+])^2 - 20.0075r^2)</td>
</tr>
<tr>
<td>I ((-2.38, -3.35))</td>
<td>(r = r(-2.1k_r + 16[H^+] - (17k_r + 71[H^+])r^2 - 0.10r^4))</td>
</tr>
</tbody>
</table>

VI. CONCLUSION

The effectiveness of methods for numerical Hopf bifurcation analysis of chemical reaction mechanisms is demonstrated by the results of the previous two sections. Codimension two Hopf bifurcations can be routinely detected and identified, thus showing that a full description of a two-parameter steady state bifurcation set of a detailed kinetic scheme is not difficult to attain.

The reader may wonder about the absence of mechanism M2 from our discussion. This version of the mechanism was proposed by Bouklakou32 and certain aspects of its steady state bifurcation structure were discussed in our earlier paper. M2 results from M0 by changing \(k_6\) from \(1 \times 10^5\) to \(2 \times 10^6\) \(M^{-1} s^{-1}\) and changing \(k_8\) from \(3.3 \times 10^3\) to \(1 \times 10^4\) \(M^{-1} s^{-1}\). Despite the seemingly minor nature of these changes, the effect on the steady state bifurcation structure is profound. The steady state bifurcation curves for this mechanism are shown in Fig. 13 for the same constraints as given above. The Hopf curve connecting the
FIG. 13. Bifurcation sets in the \((\log[H^+])\) plane for mechanism M2 for the same value of \((C(O^2^-)I-I^-_2)\) as in Fig. 3.

Takens–Bogdanov points is radically altered, and an additional closed curve of Hopf bifurcations exists.

Within the framework of this paper, it would be interesting to search for more highly degenerate Hopf bifurcation behavior in mechanism M2. By treating \(k_6\) and \(k_9\) as additional bifurcation parameters, the bifurcation behavior for an entire family of mechanisms parametrized by these two rate constants could be obtained. For example, if a codimension four point with a known unfolding could be identified in the \((k_6[H^+], k_9, k_{10})\) parameter space, the relationship between M0 and M2 would become clearer. In our opinion, although such an undertaking is very ambitious, it is the type of systematic approach most suitable to the analysis of these complicated reaction networks.

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53. The rate constant \(k_{4M_1}\) is given incorrectly as \(k_{4M_1}=k_{4M_0}\). The correct value is \(k_{4M_1}=1.6\times 10^{-3}\) s\(^{-1}\). Also, in mechanisms M0 and M2, the value of \(k_3=k_2\) was rounded to two significant digits, so \(k_{3M_0}=k_{3M_2}\) is not correct.