# Oscillations in chemical systems. IV. Limit cycle behavior in a model of a real chemical reaction

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The chemical mechanism of Field, Körös, and Noyes for the oscillatory Belousov reaction has been generalized by a model composed of five steps involving three independent chemical intermediates. The behavior of the resulting differential equations has been examined numerically, and it has been shown that the system traces a stable closed trajectory in three dimensional phase space. The same trajectory is attained from other phase points and even from the point corresponding to steady state solution of the differential equations. The model appears to exhibit limit cycle behavior. By stiffly coupling the concentrations of two of the intermediates, the limit cycle model can be simplified to a system described by two independent variables; this coupled system is amenable to analysis by theoretical techniques already developed for such systems.

## I. INTRODUCTION

In 1920, Lotka[1] devised a hypothetical set of chemical reactions (L1)–(L3)

$$A + X \rightarrow 2X \qquad (L1)$$

$$X + Y \rightarrow 2Y \qquad (L2)$$

$$Y \rightarrow P \qquad (L3)$$

which generates sustained temporal oscillations in the concentrations of intermediates X and Y during the net overall reaction $A \rightarrow P$. Such behavior is possible only if the system is maintained far from equilibrium by the exchange of reactants and products with the surroundings.

The Lotka mechanism exhibits this peculiar behavior because it includes two autocatalytic reactions, but autocatalysis is not essential for sustained oscillation. However, it is essential that at least one step in the mechanism involve feedback such that a product of the step affects its net rate other than by mass action reversibility. Such feedback leads to nonlinearity in the differential equations describing the mechanism, and the system may exhibit all of the complexities resulting from nonlinear dynamic laws.[2–4] The system must also be far from equilibrium and must be open if the oscillations are to be sustained. Ross and co-workers[5] have demonstrated that chemical systems involving a number of specific types of feedback lead to nonlinear kinetic equations and oscillatory behavior.

In 1952 Turing[6] recognized that chemical reactions with nonlinear kinetic laws could couple with diffusion to generate *spatial* patterns in the concentrations of intermediates. His theory led to a suggestion of a chemical basis of morphogenesis.

The Lotka mechanism does lead to sustained oscillations in the concentrations of intermediates, and the open system exhibits a closed trajectory in the plane of X and Y concentrations. However, the frequency and amplitude of these oscillations depend upon the initial intermediate concentrations as well as upon the kinetic constants. Moreover, if the oscillating system is perturbed, the trajectory in the *X*, *Y* plane will be shifted. In contrast, a system exhibiting *limit cycle* behavior will approach a limiting periodic behavior defined only by the kinetic constants and independent of the initi concentrations of the oscillating intermediates.

A chemical scheme exhibiting limit cycle behavic (B1)–(B4)

$$A \rightarrow X\,,$$

$$B + X \rightarrow Y + D,$$

$$2X + Y \rightarrow 3X,$$

$$X \rightarrow E,$$

has been proposed by Prigogine and co-workers[3,4] Brussels. The scheme has been called the Brusse by Tyson.[7] The net reaction is

$$A + B \rightarrow D + E.$$

Apparently this is the only known chemical scheme hibiting limit cycle behavior with only two interme species, and it has been shown by the Brussels gro to develop complex spatial and temporal structures analogous to those exhibited in biological systems. scheme has been criticized because step (B3) is thi order in the concentrations of transient intermedia but it strikingly demonstrates that chemical syster can develop very complex temporal and spatial ord

Very few homogeneous chemical systems are kn to either exhibit temporal oscillations or to develo spatial structure. Degn[8] and Nicolis and Portnow[9] reviewed the literature on the subject. The only r tion presently known to exhibit both temporal and s oscillatory structures is the cerium ion catalyzed oxidation of malonic acid by bromate in a sulfuric medium.[10] Temporal oscillations in $[Ce(IV)]/[Ce($ were first reported by Belousov[11] and development spatial structure was reported by Zhabotinskii.[12] Körös, and Noyes (FKN)[13] have developed a detaile chemical mechanism for the temporal oscillations, Field and Noyes[14] have shown that the same mecha also explains the spatial structures.

The experimental behavior of the Belousov react strongly suggests the stable limiting trajectory of termediate concentrations characteristic of a limit cycle. The present paper shows that the proposed ical mechanism can be reduced to a much simpler

 

eral mechanism that does indeed behave as a limit cycle.

## II. THE BELOUSOV MECHANISM OF FKN

The Belousov reaction mechanism of FKN can be best understood by recognizing there are two different overall processes that can occur in the system. There is little cross-talk between them because one involves only singlet species and the other is basically a radical process. Which process is dominant at a particular time or place depends upon the bromide ion concentration. Above a certain critical bromide ion concentration, Process A occurs while below this critical bromide concentration Process B is dominant. Oscillations occur because Process A consumes bromide ion and thus inevitably leads to the onset of Process B which, by indirectly producing bromide ion, returns the system to control by Process A.

Following the numbering scheme of Ref. 13, the reactions comprising Processes A and B may be written as

PROCESS A

$$Br^- + BrO_3^- + 2H^+ \rightarrow HBrO_2 + HOBr \quad (R3)$$

$$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr \quad (R2)$$

$$(Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O)\times 3 \quad (R1)$$

$$(Br_2 + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + Br^- + H^+)\times 3 \quad (R8)$$

$$2Br^- + BrO_3^- + 3H^+ + 3CH_2(COOH)_2 \rightarrow 3BrCH(COOH)_2 + 3H_2O \quad (A)$$

PROCESS B

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2^\cdot + H_2O \quad (R5)$$

$$(Ce(III) + BrO_2^\cdot + H^+ \rightarrow Ce(IV) + H_2O + HBrO_2)\times 2 \quad (R6)$$

$$2Ce(III) + BrO_3^- + HBrO_2 + 3H^+ \rightarrow 2Ce(IV) + H_2O + 2HBrO_2 \quad (G)$$

$$2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+ . \quad (R4)$$

Process A is simply the reduction of bromate ion by bromide ion through a series of oxygen transfers (2-electron reductions). Step (R3) is rate determining for the overall process. FKN demonstrated that none of the singlet oxybromine components present during Process A are thermodynamically plausible as single electron oxidants such as are required to oxidize Ce(III) to Ce(IV). Thus very little oxidation of Ce(III) to Ce(IV) occurs during Process A.

At low bromide ion concentrations, the system shifts to Process B. Bromate ion and bromous acid produce the radical species $BrO_2^\cdot$ which is a thermodynamically plausible single electron oxidant of Ce(III). The net effect of steps (R5) and (R6) is Process G, which generates bromous acid autocatalytically. The autocatalysis does not continue until the major reactants are seriously depleted because the second order destruction reaction (R4) establishes a steady state concentration of $HBrO_2$ that is still quite small. If 2(G) + (R4) is followed by the net effect of steps (R1) + (R8) of Process A, the overall reaction is that of Process B.

$$BrO_3^- + 4Ce(III) + CH_2(COOH)_2 + 5H^+ \rightarrow 4Ce(IV) + BrCH(COOH)_2 + 3H_2O . \quad (B)$$

During the initial stages of Process B when the concentration of Ce(IV) is negligibly small, step (R5) is rate determining for overall Process B, and the steady state concentration of $HBrO_2$ is $(k_{R5}/2k_{R4})[H^+][BrO_3^-]$.

The nonlinear kinetic behavior of Process G provides the feedback that is one of the requirements for sustained oscillatory behavior.

The critical features of the FKN mechanism are the competition of bromide and bromate ions for bromous acid and the autocatalytic nature of the G component of Process B. When the concentration of bromide ion is sufficiently high, nearly all bromous acid reacts with bromide ion by step (R2), and Process A describes the kinetic behavior of the system. Bromide ion is monotonically consumed during Process A, and as its concentration decreases step (R2) becomes ever less able to compete with step (R5) for bromous acid. At some point bromous acid is being produced by (R5) + 2(R6) at the same rate that it is being consumed by (R2), and at this critical bromide concentration the shift from Process A to Process B occurs. The mechanism predicts that $[Br^-]_{critical} = (k_{R5}/k_{R2})[BrO_3^-]$. FKN demonstrated experimentally that this quantity was indeed proportional only to $[BrO_3^-]$ and that the constant of proportionality was consistent with the independently estimated rate constants. Once the concentration of bromide ion has fallen to $[Br^-]_{critical}$, bromous acid is produced autocatalytically by Process G. Ce(III) is rapidly oxidized by the same process, and the remaining bromide ion is rapidly depleted by step (R2).

The Ce(IV) produced by Process B reacts according to (R9) and (R10).

$$6Ce(IV) + CH_2(COOH)_2 + 2H_2O \rightarrow 6Ce(III) + HCOOH + 2CO_2 + 6H^+ \quad (R9)$$

$$4Ce(IV) + BrCH(COOH)_2 + 2H_2O \rightarrow 4Ce(III) + HCOOH + 2CO_2 + 5H^+ + Br^- . \quad (R10)$$

Bromide ion is produced by step (R10) and sufficient of it is produced shortly after Process B is initiated to cause (R2) to again become the principal fate of bromous acid. The concentration of bromous acid drops precipitously and that of bromide ion rises as Process A again becomes dominant. This situation prevails until the concentration of bromide ion has been again reduced to $[Br^-]_{critical}$ by Process A. Generally steps (R9) and (R10) have removed the Ce(IV) produced by Process B before this occurs.

FKN estimated the following values for the rate constants of kinetically significant reactions: $k_{R3} = 2.1\ M^{-3}\ sec^{-1}$, $k_{R2} = 2\times10^9\ M^{-2}\ sec^{-1}$, $k_{R5} = 1\times10^4\ M^{-2}\ sec^{-1}$, $k_{R4} = 4\times10^7\ M^{-1}\ sec^{-1}$.

## III. THE MODEL

The FKN Belousov reaction mechanism suggested the general kinetic scheme of reactions (M1)–(M5), which can be referred to as the Oregonator:

$$A + Y \rightleftharpoons X \quad (M1)$$

$$X + Y \rightleftharpoons P \quad (M2)$$

$$B + X \rightleftharpoons 2X + Z \quad (M3)$$

$$2X \rightleftharpoons Q \quad (M4)$$

$$Z \rightleftharpoons fY. \quad (M5)$$

The simplest stoichiometric combination of the equations such that there is no net production or destruction of the intermediates X, Y, and Z is $f$(M1) + $f$(M2) + 2(M3) + (M4) + 2(M5), and this leads to the overall net reaction ($M_T$):

$$fA + 2B \rightleftharpoons fP + Q. \quad (M_T)$$

We have generalized the scheme by adding the stoichiometric factor $f$ to step (M5). This factor is significant for application to the Belousov reaction, but the calculations described below have been simplified by setting $f = 1$.

The model can be related to the FKN mechanism of the Belousov reaction by means of the identities $X \equiv HBrO_2$, $Y \equiv Br^-$, and $Z \equiv Ce(IV)$. If the reaction is treated as irreversible, and if acidity effects are included in the rate constants as defined, the final identity is $A \equiv B \equiv BrO_3^-$. If reversibility is included, designation of product species would have to be modified. The stoichiometric factor $f$ will be 1/4 if the Ce(IV) reacts only with bromomalonic acid by step (R10) and will be still smaller if reaction (R9) with malonic acid also takes place.

If the steps of the model are all assumed to be irreversible, the kinetic behavior of the Oregonator can be described by equations (Ia)–(Ic) involving the concentrations of the three intermediates:

$$dX/dt = k_{M1}AY - k_{M2}XY + k_{M3}BX - 2k_{M4}X^2, \quad (Ia)$$

$$dY/dt = -k_{M1}AY - k_{M2}XY + fk_{M5}Z, \quad (Ib)$$

$$dZ/dt = k_{M3}BX - k_{M5}Z. \quad (Ic)$$

For comparison with experiment, we adopted the situation $[BrO_3^-] = 0.06\ M$ and $[H^+] = 0.8\ M$ corresponding to the region studied experimentally. These two concentrations remained constant during the calculations, effectively treating the system as open. The numerical constants employed were

$$k_{M1} = k_{R3}[H^+]^2 = 1.34\ M^{-1}\ \text{sec}^{-1}, \quad (IIa)$$

$$k_{M2} = k_{R2}[H^+] = 1.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}, \quad (IIb)$$

$$k_{M3} = k_{R5}[H^+] = 8 \times 10^3\ M^{-1}\ \text{sec}^{-1}, \quad (IIc)$$

$$k_{M4} = k_{R4} = 4 \times 10^7\ M^{-1}\ \text{sec}^{-1}. \quad (IId)$$

The calculations arbitrarily employed the additional values

$$k_{M5} = 1\ \text{sec}^{-1}, \quad (IIe)$$

$$f = 1. \quad (IIf)$$

This selection resulted in a period comparable to experimental observations, although smaller values of both $k_{M5}$ and $f$ would better approximate the real chemical system.

Oscillatory behavior depends upon the values of both $k_{M5}$ and $f$. Regardless of the value of $f$, Y is destroyed irreversibly and no oscillations occur if $k_{M5} = 0$. On the other hand, if $f = 1$ and if $k_{M5}$ is sufficiently large, the kinetic effect is to combine steps (M3) and (M5) into the single step $B + X - 2X + Y$. This simplified model with four equations and two intermediates does not oscillate but quickly reaches a stable steady state.[15] A detailed quantitative analysis of the effect of values of $f$ and $k_{M5}$ on the appearance of oscillatory behavior in the Oregonator is presented in Sec. VII. This analysis indicates that oscillations can only occur within a certain range of $f$ values and that for each value of $f$ there is a corresponding value of $k_{M5}$ above which oscillations do not appear.

## IV. CALCULATIONS DEMONSTRATING OSCILLATORY BEHAVIOR

The equations (Ia)–(Ic) could be handled more easily and the general nature of the solution could be emphasized by casting the concentrations and time in the dimensionless variables $\alpha$, $\eta$, $\rho$, and $\tau$ and by employing the dimensionless constants $q$, $s$, and $w$. Then

$$d\alpha/d\tau = s(\eta - \eta\alpha + \alpha - q\alpha^2), \quad (IIIa)$$

$$d\eta/d\tau = s^{-1}(-\eta - \eta\alpha + f\rho), \quad (IIIb)$$

$$d\rho/d\tau = w(\alpha - \rho), \quad (IIIc)$$

where

$$[HBrO_2] \equiv X = \frac{k_{M1}A}{k_{M2}}\alpha = 5.025 \times 10^{-11}\alpha, \quad (IVa)$$

$$[Br^-] \equiv Y = \frac{k_{M3}B}{k_{M2}}\eta = 3.000 \times 10^{-7}\eta, \quad (IVb)$$

$$[Ce(IV)] \equiv Z = \frac{k_{M1}k_{M3}}{k_{M2}k_{M5}}AB\rho = 2.412 \times 10^{-8}\rho, \quad (IVc)$$

$$\text{Time} \equiv t = \tau/\sqrt{k_{M1}k_{M3}AB} = 0.1610\tau, \quad (IVd)$$

$$s = \sqrt{k_{M3}B/k_{M1}A} = 77.27, \quad (IVe)$$

$$w = k_{M5}/\sqrt{k_{M1}k_{M3}AB} = 0.1610, \quad (IVf)$$

$$q = \frac{2k_{M1}k_{M4}A}{k_{M2}k_{M3}B} = 8.375 \times 10^{-6}. \quad (IVg)$$

At the steady state where $d\alpha/d\tau = d\eta/d\tau = d\rho/d\tau = 0$ and for $f = 1$,

$$\alpha_{ss} = \rho_{ss} = 488.68, \quad (IVh)$$

$$\eta_{ss} = 0.99796. \quad (IVi)$$

Equations (III) were integrated numerically by a Runge–Kutta started predictor–corrector technique. The general behavior of the mechanism was of interest as well as how well it reproduced the actual behavior of the Belousov reaction. It was quickly determined, however, that equations (III) were "stiff"[16] and not easily integrated by the intended technique. This is often the case with differential equations describing real chemical systems containing unstable intermediates which become involved in kinetic steady states.[17] In particular the problem was with Eq. (IIIa) when $\eta(Br^-)$ was high and $\alpha(HBrO_2)$ was low. The true solution of the differential

equations is that as $\eta \rightarrow$ large values, $\alpha \rightarrow 1.0$ and $d\alpha/d\tau \rightarrow 0$, but at high $\eta$ slight errors in $\alpha$ caused by round-off propagate to produce very large (negative or positive) computed values of $d\alpha/d\tau$ when its value is actually approaching zero. Under these circumstances the integration must be carried out over exceedingly small increments if reasonable accuracy is to be maintained. Even with such small increments the computed values of $\alpha$ and $d\alpha/d\tau$ oscillate wildly about their asymptotic values.

The problem was eliminated by setting $d\alpha/d\tau = 0$ when $\alpha$ and $d\alpha/d\tau$ began to oscillate during the integration. If $d\alpha/d\tau = 0$, then a value for $\alpha$ can be calculated from Eq. (IIIa) for every $\eta$, and this value was used in the predictor and corrector for the next point in the integration. When $\eta$ fell to the point where the equations were numerically well behaved again the constraint of $d\alpha/d\tau = 0$ was lifted. This computational technique is identical to employing a steady state approximation when the concentration of $HBrO_2(\alpha)$ is of the order $10^{-6}$ that of $Br^-(\eta)$.

It has recently been pointed out[18,19] that the use of steady state approximations during the integration of stiff differential equations can lead to erroneous results. A better approach seems to be the use of the stiffly stable numerical integration techniques of Gear.[20] The results reported here have been spot checked using a recently acquired program[21] employing these techniques. The results indicate that the steady state assumption as used in this work does not lead to appreciable error in the analysis of the Oregonator.

Figure 1 shows the results of the numerical integration plotted as the original Belousov reaction concentration variables vs time. The intermediate concentrations are clearly oscillatory in time, and the plots are qualitatively of the same form as the experimentally observed oscillations in the Belousov reaction. (See Ref. 13, Figs. 1–6). The critical bromide ion concentration where the shift from Process A to B occurs is read from the $\log[Br^-]$ plot in Fig. 1 as $3.0\times10^{-7}$ $M$, which is exactly the value calculated from $[Br^-]_{critical} = (k_{R5}/k_{R2})[BrO_3^-]$ for $[BrO_3^-] = 6.0\times10^{-2}$ $M$. The period of the oscillations is 48.75 sec, which is very similar to that obtained experimentally for the same concentrations of bromate and hydrogen ion. Somewhat better quantitative agreement between the calculated and experimental oscillations could be obtained by using a value of $k_{M5}$ about ten times less than that actually used, but behavior in this region is not critically dependent upon the value of $k_{M5}$.

The concentrations $\alpha$, $\eta$, and $\rho$ define a three dimensional phase space through which the oscillating reaction traces a closed trajectory. That trajectory can be illustrated by plots of two dimensional projections. Figure 2 is such a plot relating $\log\alpha(HBrO_2)$ to $\log\eta(Br^-)$. Arrows indicate the direction of time evolution, and the heavy trace corresponds to the trajectory of the system during stable oscillations. The numbers on the heavy trace indicate the relative times in a cycle of length $\tau = 302.9$. The comparatively small region in which $\log\eta > 1$ and $\log\alpha \approx 0$ covers most of the time scale in Fig. 1; throughout most of this region the calculated bromous acid concentration from Fig. 2 is the same as the steady state concentration calculated from

$$[HBrO_2]_A = (k_{R3}/k_{R2})[H^+][BrO_3^-] = 5.025\times10^{-11}\ M.$$

Process A is dominant throughout this region.

The region with $\log\eta < 0$ corresponds to bromide ion less than $[Br^-]_{critical}$ and Process B becomes dominant. Because bromide ion is produced so rapidly by step (R10) when Process B becomes dominant, (R2) is never totally suppressed and the concentration of bromous acid approaches but does not quite attain the steady state value of

$$[HBrO_2]_B = (k_{R5}/2k_{R4})[H^+][BrO_3^-] = 6.0\times10^{-6}\ M\ .$$

The maximum bromous acid concentration attained in Fig. 2 is $5.86\times10^{-6}$ $M$, but this is still more than $10^5$ times the concentration present when the system is controlled by Process A.

Figure 3 is a similar projection plot relating $\log\rho(Ce(IV))$ to $\log\eta(Br^-)$. The third orthogonal projection of $\alpha$ against $\rho$ is derivable from the other two and is not presented here. Comparison of Figs. 1, 2, and

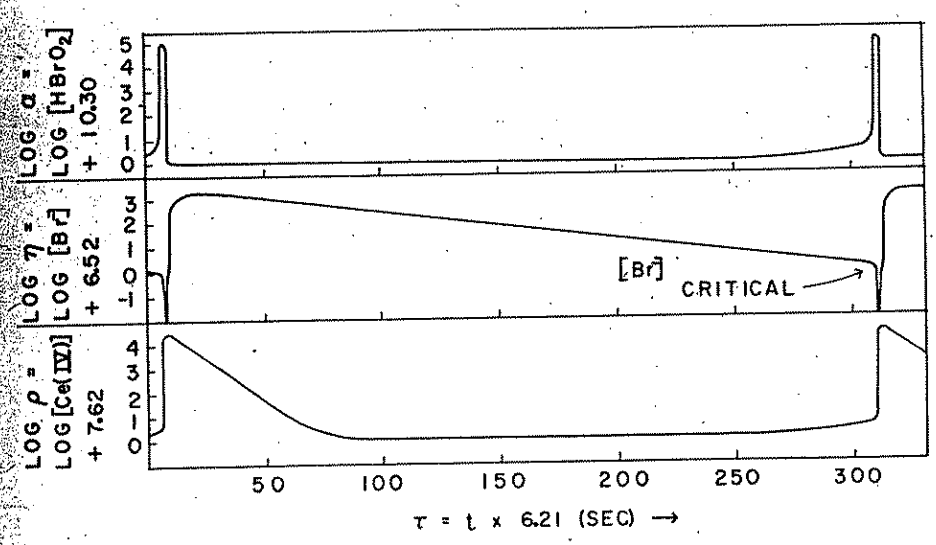


FIG. 1. Traces of log[Ce(IV)] ($\rho$), log[B ($\eta$) and log[$HBrO_2$] ($\alpha$) vs time ($\tau$) obtain by numerical integration of Eqs. III, whi result from the Field, Körös, and Noyes mechanism for the Belousov reaction. T integration used $f = 1$. Process A is occu ring during the long stretches when HBr ($\alpha$) is low and Process B is occurring wi the sharp spikes of $HBrO_2$ ($\alpha$) appear.

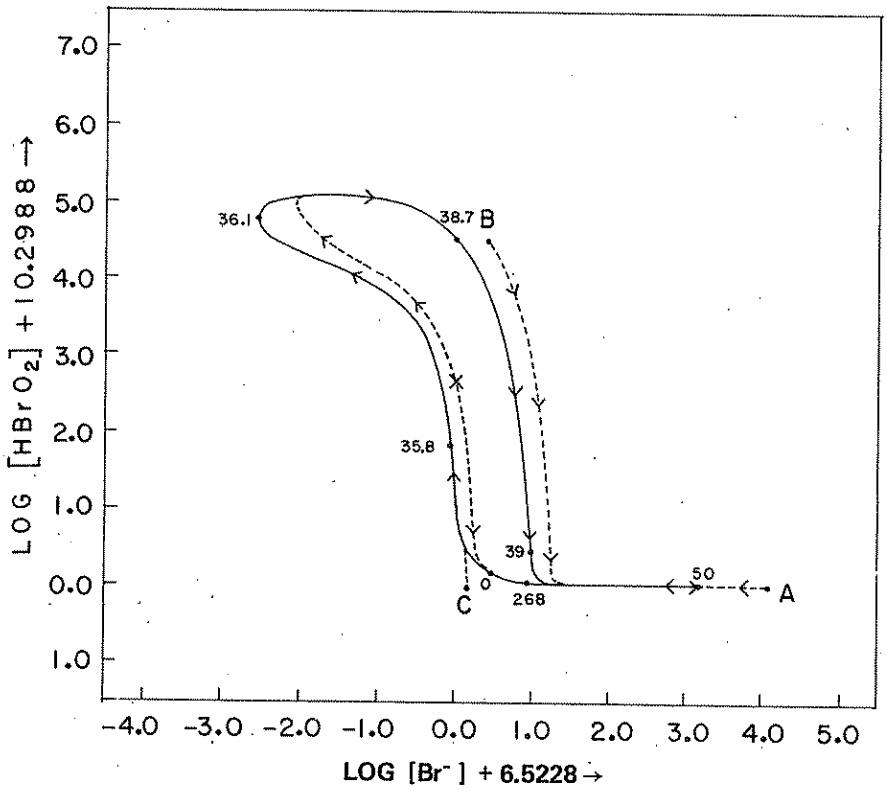


FIG. 2. Phase plane plot of $\log[HBrO_2]$ ($\alpha$) vs $\log[Br^-]$ ($\eta$) obtained by numerical integration of Eqs. (III). The solid line indicates the unique limit cycle solution for the kinetic constants used and the dashed lines indicate the path of approach to the limit cycle of systems not originally on it. The cross indicates the steady state, and the arrowheads indicate the direction of time evolution. Points A, B, and C correspond to the same points in Fig. 3, and the numbers indicate times in the cycle. $\tau = 302.9$ for the entire cycle.

3 demonstrates that the system does not traverse the phase space at a constant velocity.

## V. LIMIT CYCLE BEHAVIOR

The calculations described in the previous section and illustrated in Figs. 1–3 offer strong support for the general validity of the mechanism of the Belousov reaction proposed by Field, Körös, and Noyes.[13] The oscillations observed in that reaction are so stable that it seemed probable the mechanism illustrated true limit cycle behavior.

When integrations were carried out for more than one cycle, successive trajectories followed each other to within the 0.1 precision of the calculation. The dashed

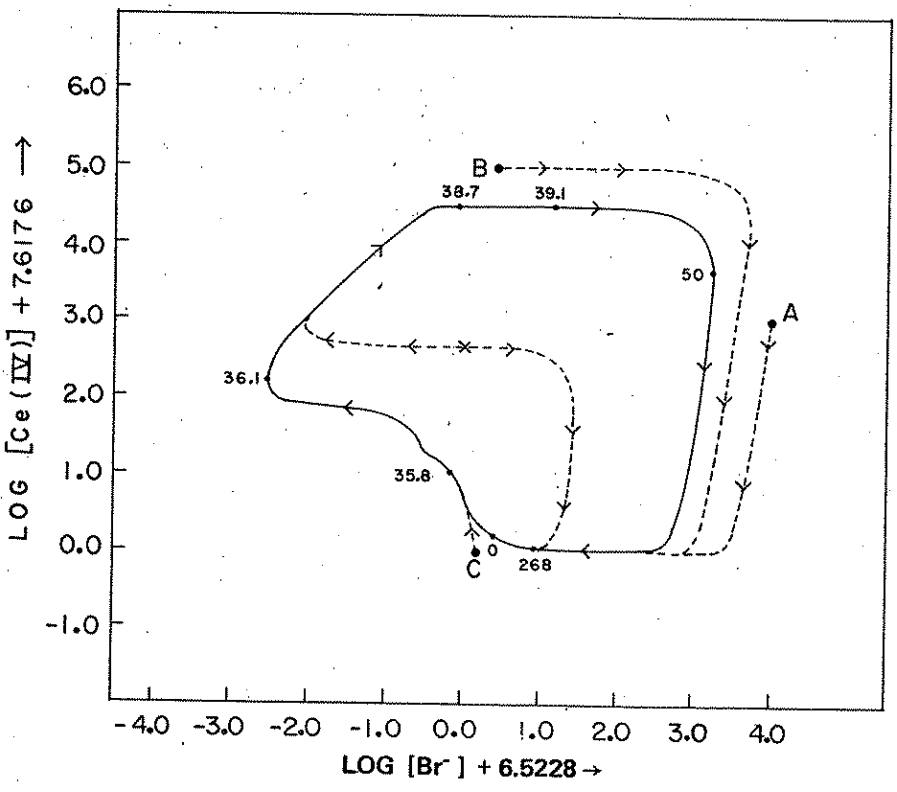


FIG. 3. Phase plane plot of $\log[Ce(IV)]$ ($\rho$) vs $\log[Br^-]$ ($\eta$) obtained by numerical integration of Eqs. (III). The solid line indicates the unique limit cycle solution for the kinetic constants used and the dashed lines indicate the path of approach to the limit cycle of systems not originally on it. The cross indicates the steady state, and the arrowheads indicate the direction of time evolution. Points A, B, and C correspond to the same points in Fig. 2, and the numbers indicate times in the cycle. $\tau = 302.9$ for the entire cycle.

trajectories in Figs. 2 and 3 demonstrate that systems started at points not on the cycle quickly approach the same trajectory. As a still more severe test, it was shown that the steady state position itself was unstable. If the system were started exactly at the steady state, round-off error was sufficient to perturb the system so that it left the steady state and approached the same trajectory. A system already on the limiting trajectory is clearly stable to perturbation, unlike the situation in the Lotka mechanism, (L1)–(L3).

It therefore appears that the solution to Eqs. (III) under the conditions employed here is a true limit cycle that not only demonstrates sustained oscillatory behavior but is also "ergodic" in the sense that the system eventually evolves to the same periodic trajectory regardless of the initial condition.

## VI. STIFFLY COUPLED APPROXIMATION

Although the Oregonator (M1)–(M5) exhibits limit cycle behavior, it suffers from the disadvantage that the three intermediates X, Y, and Z are involved. As Tyson[7] has commented, the Brusselator model [Eqs. (B1)–(B4)] involves only two intermediates, and a powerful mathematical machinery has been developed for limit cycle behavior of differential equations describing such two dimensional systems. When the state of a system can be described by a point in a phase plane, the well known theorems of Poincaré and Bendixson are applicable. We know of no analogous qualitative (topological) results for more than two independent variables, and the investigation described above has been purely numerical.

For purposes of mathematical analysis, the Oregonator can be converted to a model of two independent variables by postulating that bromous acid is always present in a steady state concentration determined by the concentration of bromide ion. Then $k_{M2} \gg k_{M1}$ and $k_{M4} \gg k_{M3}$. Such a stiff coupling approximation is equivalent to setting $d\alpha/d\tau = 0$ in Eq. (IIIa). The results in Fig. 1 indicate that this is a reasonable approximation throughout much of the cycle. The state of the system is then described by Eqs. (IIIb) and (IIIc) with the additional requirement of Eq. (V).

$$\alpha = \{(1-\eta) + [(1-\eta)^2 + 4q\eta]^{1/2}\}/2q. \qquad (V)$$

Figure 4 represents the solution of Eq. (V) and can be compared to Fig. 2. The solution is restricted to the limits actually attained by the limit cycle trajectory.

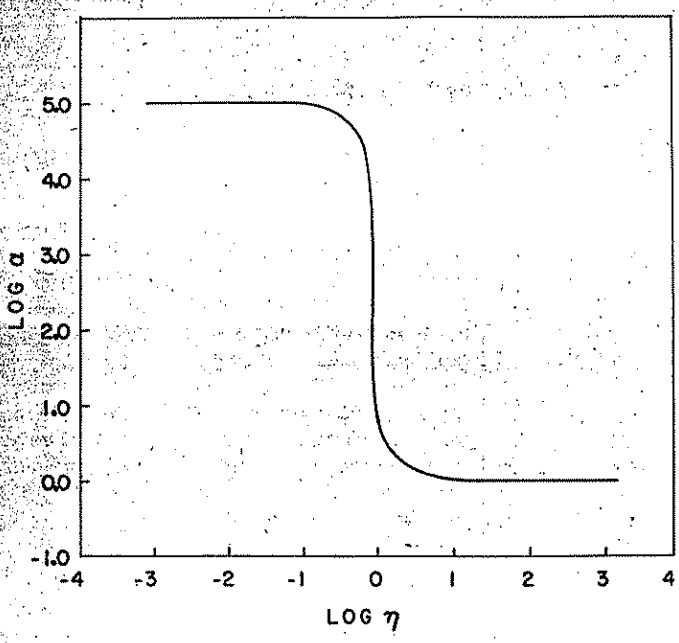


FIG. 4. Comparison of log $\alpha$ and log $\eta$ when they are linked through Eq. (V). This figure is comparable to the phase plane projection plot of Fig. 2.

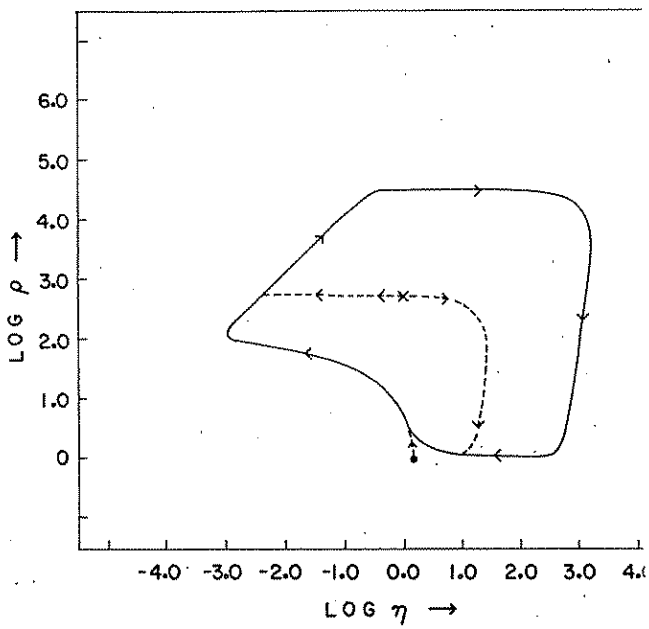


FIG. 5. Phase plane plot of log $\rho$ vs log $\eta$ obtained by integrating Eqs. (IIIb) and (IIIc) with $\alpha$ linked to $\eta$ through Eq. (V). The steady state is indicated by the cross and the limit cycle the solid line. The arrowheads indicate the direction of time evolution.

Figure 5 illustrates phase plane trajectory calculations for the system defined by Eqs. (IIIb), (IIIc), and (V). The dashed lines indicate that this system also exhibits limit cycle behavior even when Eq. (V) restricts it to two independent variables. The steady state in Figs. 4 and 5 is of course the same as that in Figs. 2 and 3.

## VII. LIMITING VALUES OF PARAMETERS

With the exception of the stoichiometric factor $f$ and the rate constant $k_{M5}$, values for all of the parameters in the Oregonator were assignable by analogy to the Field–Belousov reaction mechanism. The numerical results described above were obtained with $f = k_{M5} = 1$, but the range of values of these parameters for which the Oregonator exhibits oscillatory behavior is also of considerable interest. In order for a chemical system to exhibit oscillations, it is necessary that its steady state be unstable with respect to small perturbations. Such instability, however, does not guarantee limit cycle behavior. The response of a steady state to very sma

perturbations can be investigated by means of a normal mode analysis.[3,4] When the steady state of the rate equations (IIIa)–(IIIc) is subjected to a perturbation of the form

$$\alpha = \alpha_{ss} + Ae^{\lambda t}, \tag{VIa}$$

$$\eta = \eta_{ss} + Ne^{\lambda t}, \tag{VIb}$$

$$\rho = \rho_{ss} + Pe^{\lambda t}, \tag{VIc}$$

and the result linearized, the variational equation (VId) is obtained.

$$\lambda^3 - (a - c - w)\lambda^2 - [ac + bd + (a - c)w]\lambda - (ac + be + bd)w = 0, \tag{VId}$$

$$a = s(1 - 2\alpha_{ss}q - \eta_{ss}), \tag{VIe}$$

$$b = s(1 - \alpha_{ss}), \tag{VIf}$$

$$c = (1 + \alpha_{ss})/s, \tag{VIg}$$

$$d = -\eta_{ss}/s, \tag{VIh}$$

$$e = f/s, \tag{VIi}$$

$$\alpha_{ss} = \{(1 - f - q) + [(q + f - 1)^2 + 4(f + 1)q]^{1/2}\}/2q, \tag{VIj}$$

$$\approx (1 - f)/q \qquad f < 1,$$

$$\approx \sqrt{2/q} \qquad f \approx 1,$$

$$\approx (f + 1)/(f - 1) \qquad f > 1,$$

$$\eta_{ss} = f\alpha_{ss}/(1 + \alpha_{ss}). \tag{VIk}$$

A sufficient condition for instability of the steady state of Eqs. (IIIa)–(IIIc) to very small perturbations is that the coefficient of the $\lambda$ term be negative, i.e.,

$$Q \equiv -[ac + bd + (a - c)w] < 0. \tag{VII}$$

Since the values of both $\alpha_{ss}$ and $\eta_{ss}$ depend upon $f$ [Eqs. (VIj) and (VIk)] and the value of $w$ depends upon $k_{M5}$, $Q$ must depend upon both $f$ and $k_{M5}$. Figure 6 shows the values of $k_{M5}$ and $f$ for which $Q = 0$. For systems within the shaded region, the steady state is necessarily unstable. We have subsequently applied both necessary and sufficient criteria and find $k_{M5}$ at the transition between stability and instability is never more than 4% greater than indicated in Fig. 6. At larger values of $k_{M5}$, the steady state is stable to small perturbations but may be unstable to larger ones.

The results of the normal mode analysis can be rationalized qualitatively by noting the Oregonator oscillates because the concentration of $X$ is switched between close approximations to the limiting values of $X_{min}$ and $X_{max}$ of Eqs. (VIIa)–(VIIb):

$$X_{min} = k_{M1}A/k_{M2} = 8.38 \times 10^{-10}A, \tag{VIIa}$$

$$X_{max} = k_{M3}B/2k_{M4} = 1 \times 10^{-4}B. \tag{VIIb}$$

These equations are equivalent to $\alpha_{min} = 1$ and $\alpha_{max} = 1/q$. Switching occurs whenever $Y$ passes through $Y_{crit}$.

$$Y_{crit} = k_{M3}B/k_{M2} = 5 \times 10^{-6}B. \tag{VIIc}$$

Steady-state concentrations of $X$ and $Y$ are given by Eqs. (VIId)–(VIIe):

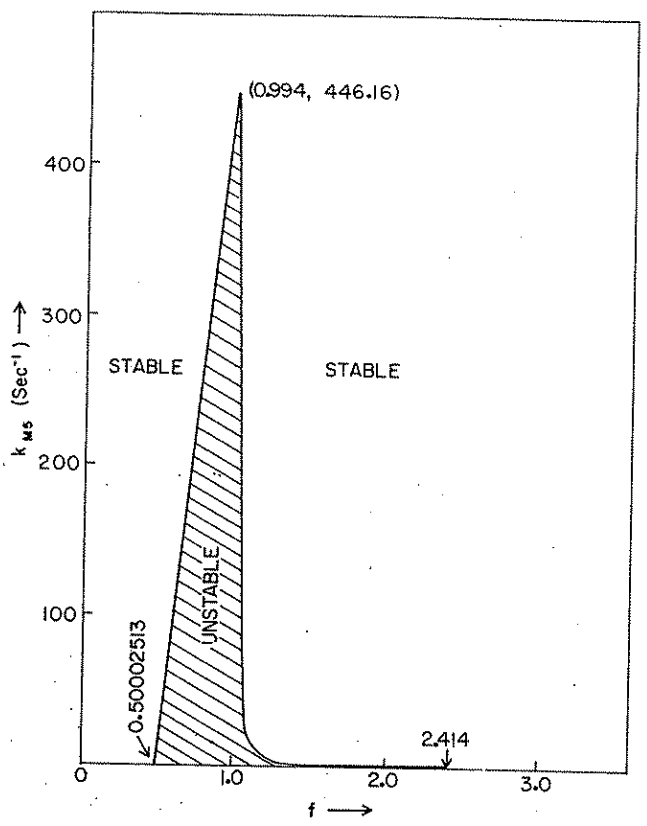


FIG. 6. Normal mode analysis results indicating the region of instability of the Oregonator steady state. The solid line indicates the values of $k_{M5}$ and $f$ for which $Q = 0$. The steady state is unstable to very small perturbations only in the hatched area. Numerical values of the limit points are given.

$$X_{ss} = (k_{M1}A/k_{M2})\,\alpha_{ss}, \tag{VIId}$$

$$Y_{ss} = \frac{fk_{M3}BX_{ss}}{k_{M1}A + k_{M2}X_{ss}}. \tag{VIIe}$$

If $Y$ and $Y_{crit}$ are on the same side of $Y_{ss}$, the system will always pass through $Y_{crit}$ during approach to the steady state, and $X$ will be switched. If $Y$ and $Y_{crit}$ are on opposite sides of $Y_{ss}$, undamped oscillations will occur only if $Y$ overshoots $Y_{ss}$ enough to attain $Y_{crit}$.

As is shown below, the $Y$ overshoot of $Y_{ss}$ decreases as $k_{M5}$ becomes larger. Comparison of Eqs. (VIIc) and (VIIe) indicates that $Y_{crit}$ and $Y_{ss}$ will be closest when $f$ is near unity. Figure 6 demonstrates that oscillations do indeed occur over the widest range of $k_{M5}$ values when $f$ is in this region. When $f$ differs much from unity in either direction, oscillations become impossible for any value of $k_{M5}$.

If $f$ is greater than unity, $Y_{ss} > Y_{crit}$ and oscillations will occur only if $Y$ continues to decrease after it has passed $Y_{ss}$. Equations (M1)–(M4) consume $Y$ irreversibly, and $Y$ will overshoot $Y_{ss}$ until $Z$ can build up enough to regenerate $Y$ by (M5). The greater the value of $k_{M5}$, the faster $Y$ will be produced and the less will be the overshoot. We can therefore see why the system with $f > 1$ is stable to oscillation except at small values of $k_{M5}$.

If $f$ is less than unity, $Y_{ss} < Y_{crit}$ and oscillations will occur only if $Y$ continues to increase after it has passed $Y_{ss}$. Such increase requires a considerable reservoir

of $Z$ when $Y$ attains $Y_{ss}$ and production of more $Z$ is switched off; such a reservoir will exist only if $k_{M5}$ is small so that the system had to spend a sufficient time with $X$ near $X_{max}$.

The argument based on overshoot is not identical to the one that generated Fig. 6, but the conclusions are qualitatively similar.

The above analysis also permits an explanation of the induction period observed when malonic acid is the only organic species initially present. Virtually all of the cerium (IV) is reduced without generating bromide ion, and the $f$ factor is very small. However, the CD portion of Fig. 1 in Ref. 13 suggests a damped oscillation during approach to the low steady state concentration of bromide ion following the first rapid production of cerium (IV). As more and more bromomalonic acid is produced, $f$ steadily increases while $k_{M5}$ changes comparatively little. The normal mode analysis indicates that when $f$ becomes sufficiently large the existing steady state becomes unstable. A transient perturbation will then drive bromide ion above $Y_{crit}$ and cause bromous acid (X) to switch before cerium (IV) (Z) can follow. The limit cycle oscillations will then commence.

A potential flaw in this argument is that the stoichiometry of reaction (R10) implies a maximum possible $f$ of 0.5 while Fig. 6 indicates the steady state is stable unless $f > 0.5$. However, reaction (R10) is an overall stoichiometry. We have found[22] that sudden addition of cerium (IV) to bromoalonic acid initially produces *one* bromide ion for each equivalent of oxidant consumed; stoichiometry then changes with time. We are still studying these complicated processes, which are important to the overall description of the system but not to the basic principles that drive the Oregonator.

## VIII. SUMMARY AND SUGGESTIONS FOR FURTHER WORK

The Oregonator (M1)–(M5) is derived from the more complicated FKN mechanism for the Belousov reaction. It is not intended that it reproduce in detail the behavior of the Belousov reaction, but it is intended that it possess the unique features that lead to oscillations in that reaction. We have shown here that the model is easily subject to numerical analysis and that it exhibits the important oscillatory limit cycle behavior already demonstrated experimentally. We have also shown that a stiff coupling of the concentration of X to that of Y generates a system of two independent variables that permits already existing theoretical developments to be applied to a system having experimental precedent.

Several additional types of calculation immediately suggest themselves. It is well known[12,14,23] that the Belousov reaction also generates spatial patterns of moving bands, and it should be quite feasible to couple diffusion to the model developed here. Dependence of behavior on the parameters $k_{M5}$ and $f$ should be explored more thoroughly than has been done.

Finally, it is well known[3,4] that oscillatory behavior requires the system to be far from equilibrium. We have clearly met that restriction by treating all reactions as irreversible. If reversibility were added to the calculations, either with or without the stiff coupling approximation, and the concentrations of A and B were allowed to be depleted, then it would be possible to explore the interesting behavior as an initially almost stable oscillating system degenerates to the required monotonic approach to ultimate equilibrium.

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[1] A. J. Lotka, J. Am. Chem. Soc. **42**, 1595 (1920).
[2] N. Minorsky, *Nonlinear Oscillations* (Van Nostrand, Princeton, NJ, 1962).
[3] P. Glandsdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations* (Wiley, New York, 1971).
[4] G. Nicolis, Advan. Chem. Phys. **19**, 209 (1971).
[5] P. J. Ortoleva and J. Ross, J. Chem. Phys. **55**, 4378 (1971); **56**, 287, 293, 4397 (1972). R. G. Gilbert, H. Hahn, P. J. Ortoleva, and J. Ross, "Chemical Oscillations and Multiple Steady States Due to Variable Boundary Permeability" (to be published). A. Nitzan and J. Ross, "Oscillations, Multiple Steady States and Instabilities in Illuminated Systems" (to be published).
[6] A. M. Turing, Phil. Trans. R. Soc. Lond. B **273**, 37 (1952).
[7] J. J. Tyson, J. Chem. Phys. **58**, 3919 (1973).
[8] H. Degn, J. Chem. Ed. **49**, 302 (1972).
[9] G. Nicolis and J. Portnow, Chem. Rev. **73**, 365 (1973).
[10] Some substitutions are possible for the cerium ion and malonic acid, but the requirement for bromate ion is specific. The sulfuric acid is about 1*M*. See Ref. 13 for further details.
[11] B. P. Belousov, Sb. Ref. Radiats. Med., 1958, Medgiz, Moscow, 145 (1959).
[12] A. M. Zhabotinskii, *Oscillatory Processes in Biological and Chemical Systems* (Science Publ., Moscow, 1967), p. 149; A. N. Zaikin and A. M. Zhabotinsky, Nature **225**, 535 (1970).
[13] R. J. Field, E. Körös, and R. M. Noyes, J. Am. Chem. Soc. **94**, 8649 (1972).
[14] R. J. Field and R. M. Noyes, Nature **237**, 390 (1972). A quantitative model is in preparation.
[15] R. M. Mazo, University of Oregon (unpublished results).
[16] C. F. Curtiss and J. O. Hirschfelder, Proc. Natl. Acad. Sci. (USA) **38**, 235 (1952).
[17] J. O. Hirschfelder, J. Chem. Phys. **26**, 271 (1957).
[18] D. Edelson, J. Comput. Phys. **11**, 455 (1973).
[19] R. J. Gelinas, J. Comput. Phys. **9**, 222 (1972).
[20] C. W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations* (Prentice-Hall, Englewood Cliffs, NJ, 1971), p. 209ff.
[21] A. C. Hindmarsh, Lawrence Livermore Laboratory, Livermore, California 94550.
[22] J. J. Jwo, University of Oregon (unpublished results).
[23] A. T. Winfree, Science **175**, 634 (1972).