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# Diffusion and chemical oscillations—theory and calculations on a mechanism for the bromate–cerium–malonic acid system

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An approach to the calculation of the boundary of stability of chemically oscillating systems with diffusion has been developed. The method uses the fact that the Routh–Hurwitz stability criterion has an absolute minimum of zero at the boundary of stability. The condition for this minimum can be used to obtain the shape of the boundary of stability in concentration space, the wavelength and frequency of the undamped perturbation, and the oscillating normal modes of the reaction system. The method is developed using a model mechanism derived from the one discussed by Glansdorff and Prigogine for the bromate–cerium–malonic acid instability. The difficulties to be encountered if this method is extended to the much more complicated mechanism of Noyes, Field, and Körös appear great. Calculations done for the model mechanism produced a boundary of stability with a very complex shape which was dependent on only two parameters and would serve to verify the reaction mechanism.

## I. INTRODUCTION

For some systems of chemical reactions a nonequilibrium steady state may be unstable if the system is constrained far enough from equilibrium. This paper is concerned with one type of such steady state: that whose instability arises from a feedback mechanism inherent in the reaction kinetics. Instabilities of this type are capable of producing time oscillations in the concentrations of some molecules or ions. These particles may also be periodically distributed in space resulting in a travelling wave of concentration.

An elegant and elaborate theoretical analysis of these instabilities has been carried out by Glansdorff, Prigogine, and co-workers.<sup>1</sup> As the number of chemical reactions increases and the number of chemical species which must be included in the analysis increases, the difficulty in determining the stability of a reaction mechanism increases dramatically. If diffusion is included, as is necessary for the spacial type of instability, a further large increase in complexity occurs. Much work therefore remains to be done if insight is to be gained into complex reaction systems from a theoretical standpoint.

The number of known experimental systems exhibiting this type of instability is at present very small. The bromate–cerium–malonic acid system is by far the best understood,<sup>2</sup> yet a complete stability analysis of this system would be difficult because of the large number of chemical species and reactions that are involved. An iodide–hydrogen peroxide system is also known to oscillate<sup>3</sup> and several possible biochemical reaction systems which probably are unstable have been pointed out as well.<sup>4</sup>

This paper presents a thorough stability analysis which includes diffusion of a model system processing both time oscillation instabilities and a spacial wave instability. The model has only five reactions and four

independent unconstrained particle concentrations. Yet, the increase in mathematical complexity compared with a similar calculation on a model with only two fluctuating concentrations is remarkable. To the author's knowledge this is the most complex model system which has yielded to such a thorough analysis. It is hoped that the methods used here can be refined until systems as complicated as those encountered experimentally may be treated.

In its initial stages the stability calculation follows the approach of Glansdorff and Prigogine. First the steady states are determined, then the equations for the evolution of perturbations from the steady state are written down. The steady states are stable only if all perturbations from them die out. Mathematically this implies that the real parts of all the eigenvalues of a matrix are negative. The boundary of the region of stability may then be determined by solving the condition that the real parts of all but one eigenvalue are negative and the one eigenvalue is purely imaginary. This condition, when diffusion is included, becomes rapidly more difficult to solve as the number of reactions and variable concentrations increases. The strategy used to solve this is given in detail. Once the boundary of stability has been determined the wavelength and frequency of the unstable perturbation may easily be calculated. This should be close to the wavelength and frequency of the concentration variations just across the stability boundary which would be observable in an experimental system. The shape of the boundary of stability is unexpectedly complicated considering the simplicity of the model used.

The model was chosen to represent the mechanism discussed by Glansdorff and Prigogine<sup>5</sup> for the bromate–cerium–malonic acid system. It could be extended to match the actual mechanism<sup>2</sup> by adding another six reactions and three intermediates while omitting the reactions of the species called Z. An effort is being made

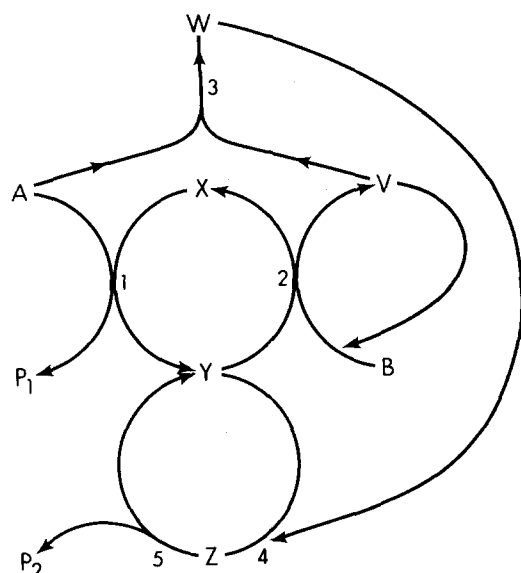


FIG. 1. Diagrammatic representation of the model reaction system. All numbered reactions occur in the forward direction only (indicated by arrows) with kinetics illustrated.  $A$ ,  $B$ ,  $C \equiv X + Y + Z$  are constraints.

to extend this analysis toward a more realistic model of the bromate instability.

## II. THE REACTION SYSTEM

The model consists of the following five reactions:

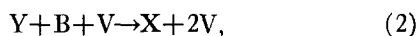
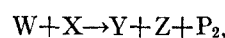
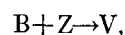


Figure 1 displays the structure of this system. The correspondence with the model discussed by Glansdorff and Prigogine for the bromate–cerium–malonic acid system is as follows.  $A$  and  $B$  are malonic acid and bromate;  $X$ ,  $Y$ , and  $Z$  are the three forms of cerium  $Ce^{4+}$ ,  $Ce^{3+}$ , and complexed cerium;  $V$  represents bromine produced in the autocatalytic oxidation of  $Ce^{3+}$  [Reaction (2)];  $W$  is brominated malonic acid;  $P_1$  and  $P_2$  are reaction products. Reaction (2) has been made autocatalytic in the simplest way possible by introducing direct feedback from  $V$ . The only other equally simple method to introduce such feedback would be via  $X$  which would not be plausible for the bromate system.

The mechanism of Noyes, Field, and Körös for the bromate–cerium–malonic acid system<sup>6</sup> uses  $Br^-$  to turn on and off the autocatalytic oxidation of cerium [Reaction (2)]. Their mechanism would be represented very crudely by replacing Reactions (4) and (5) with

the reactions



where  $Z$  now represents  $Br^-$  instead of complex. However, a detailed model of the NFK mechanism would require three more fluctuating concentration variables and many more reactions. Since the present model is not yet of experimental value the mathematics has been simplified by avoiding the complications of stoichiometry.

The diffusion of “ionic cerium”  $X$  and  $Y$  as well as “bromine”  $V$  has been included in the model. The results will show that the diffusion of  $Y$  destabilizes certain steady states with respect to wavelike perturbations; however, the diffusion of  $V$  will stabilize these states again. In the NFK mechanism  $HBrO_2$  plays the same role that  $Y$  does in this model.<sup>7</sup>

All reactions are taken only in the forward direction. The total concentration of cerium,

$$C = X + Y + Z, \quad (6)$$

is constant for all stable steady states being considered. This and  $A$  and  $B$  are considered to be the constraints on the system. Then the remaining independent variables are  $V$ ,  $W$ ,  $Y$ ,  $Z$ , which evolve as follows:

$$\dot{V} = k_2 B V Y - k_3 A V + D \nabla^2 V, \quad (7)$$

$$\dot{W} = k_3 A V - k_4 W Y, \quad (8)$$

$$\dot{Y} = k_1 A (C - Y - Z) - k_2 B V Y - k_4 W Y + k_5 Z + D' \nabla^2 Y, \quad (9)$$

$$\dot{Z} = k_4 W Y - k_5 Z. \quad (10)$$

These dynamical equations have only one steady state for which  $V$  or  $Y$  are not zero.<sup>8</sup> This steady state is given by

$$(V_0, W_0, Y_0, Z_0) = (\gamma/d, b\gamma, 1, a\gamma) \times k_3 a / k_4 b,$$

where dimensionless variables have been defined:

$$a = (k_1/k_5) A, \quad (11)$$

$$b = (k_2/k_4 d) B, \quad (12)$$

$$c = (k_4/k_5) C, \quad (13)$$

$$d = k_3/k_1, \quad (14)$$

$$\gamma = \frac{bc/a - 1}{1 + a}. \quad (15)$$

Since the rate of production of  $V$  by reaction is  $(k_2 B Y - k_3 A) V$ , it will either grow or decay exponentially according to the sign of  $k_2 B Y - k_3 A$ . If  $V$  decays, Reaction (2) slows and  $Y$  reaches a maximum of  $C$ . Hence if

$$k_3 A > k_2 B C, \quad (16)$$

all reactions will come to a stop because Reaction (3) is

depleting  $V$  faster than the maximum rate that Reaction (2) can produce it. From (16) a necessary condition for a nonzero steady state to exist is<sup>9</sup>

$$bc \geq a \quad (17)$$

or

$$\gamma \geq 0. \quad (18)$$

Henceforth the variable  $c$  will be replaced by  $\gamma$ , making

$$\mathbf{M} = \begin{pmatrix} D\nabla^2 & 0 & k_2BV_0 & 0 \\ k_3A & -k_4Y_0 & -k_4W_0 & 0 \\ -k_2BY_0 & -k_4Y_0 & -k_1A - k_2BV_0 - k_4W_0 + D'\nabla^2 & k_5 - k_1A \\ 0 & k_4Y_0 & k_4W_0 & -k_5 \end{pmatrix}. \quad (20)$$

This linearized equation is only valid if  $\Delta\mathbf{v}$  is sufficiently small. Since the arbitrary  $\Delta\mathbf{v}$  may be represented as an arbitrary sum of perturbations of the form

$$\mathbf{A} \exp(i\mathbf{k}' \cdot \mathbf{r} + \omega' t), \quad (21)$$

the system is stable if and only if every small perturbation of this form decays. Substituting this form of  $\Delta\mathbf{v}$  in (19), and considering that no generality is lost if  $\mathbf{A}$  is an eigenvalue of the resulting matrix (since such eigenvalues span the space of all possible  $\mathbf{A}$ 's) we find that  $\omega'$  must be the corresponding eigenvalue. The characteristic equation which determines  $\omega'$  can be written using a dimensionless  $\omega$  and  $k$  as follows:

$$\begin{vmatrix} \omega + ek^2 & 0 & -a\gamma & 0 \\ -ad & \omega + a/b & a\gamma & 0 \\ ad & a/b & \omega + a + 2a\gamma + k^2 & a-1 \\ 0 & -a/b & -a\gamma & \omega + 1 \end{vmatrix} = 0, \quad (22)$$

where

$$k = (D'/k_5)^{1/2} |\mathbf{k}'|, \quad (23)$$

$$\omega = \omega'/k_5, \quad (24)$$

$$e = D/D'. \quad (25)$$

The parameter  $e$  specifies the relative rates of diffusion of  $V$  and  $Y$ . The perturbation will decay if the real part of  $\omega$  is negative; the system is stable if every perturbation decays. That is, for every  $k$  all four eigenvalues  $\omega$  must have negative real parts. Conversely the system is not stable if there exists a value of  $k$  which has an eigenvalue  $\omega$  with a nonnegative real part. The boundary of stability occurs when the real part of an eigenvalue first becomes zero for some value of  $k$ .

It is interesting to note that by using dimensionless parameters the seven physical parameters  $k_1 \cdots k_5, D, D'$  have been reduced to the two parameters  $d$  and  $e$ . The

the dimensionless constraints on the system  $a, b$ , and  $\gamma$ , so that the physically realistic values of these parameters are taken in the positive octant of  $ab\gamma$  space.

Dynamical Eqs. (7)–(10) may be written for an arbitrary small perturbation  $\Delta\mathbf{v}$  from the steady state  $\mathbf{v}_0$  as

$$\Delta\dot{\mathbf{v}} = \mathbf{M}\Delta\mathbf{v}, \quad (19)$$

where  $\Delta\mathbf{v} = (\Delta V, \Delta W, \Delta Y, \Delta Z)^t$ ,

five parameters which have been eliminated only affect the scaling of  $A, B, C, \omega'$ , and  $k'$ . The problem now is to find the boundary of the stable region in  $ab\gamma$  space for chosen values of  $d$  and  $e$ . To do this one must examine Eq. (22) to determine if for any  $k$  there is a root  $\omega$  with zero real part when the other roots have negative real parts and all other  $k$ 's have roots with only negative real parts.

### III. THE STABILITY CONDITION

An explicit stability condition may be constructed from Eq. (22). The determinant is first multiplied out to give the characteristic equation

$$b\omega^4 + \bar{\alpha}_1\omega^3 + \bar{\alpha}_2\omega^2 + \bar{\alpha}_3\omega + \bar{\alpha}_4 = 0, \quad (26)$$

where

$$\bar{\alpha}_1 = \alpha_1 + sb + tb, \quad (27)$$

$$\bar{\alpha}_2 = \alpha_2 + s(b+a) + t[b+a(1+b+2b\gamma)] + stb, \quad (28)$$

$$\bar{\alpha}_3 = \alpha_3 + sa + t[a(1+b+b\gamma) + a^2(1+\gamma+b\gamma)] + st(b+a), \quad (29)$$

$$\bar{\alpha}_4 = \alpha_4 + ta^2(1+\gamma) + sta, \quad (30)$$

$$\alpha_1 = b + a(1+b+2b\gamma), \quad (31)$$

$$\alpha_2 = a(1+b+b\gamma) + a^2(1+\gamma+b\gamma+b\gamma d), \quad (32)$$

$$\alpha_3 = a^2(1+\gamma+b\gamma d) + a^3(2\gamma d), \quad (33)$$

$$\alpha_4 = a^3(\gamma d) + a^4(\gamma d), \quad (34)$$

$$s = k^2, \quad (35)$$

$$t = ek^2. \quad (36)$$

The characteristic equation has been multiplied through by  $b$  to eliminate fractions. The coefficients have been organized into polynomials in  $s$  and  $t$  which have been expanded in turn in powers of  $a$ .

The necessary and sufficient conditions that the roots of a polynomial such as (26) all have negative real

parts are the Routh–Hurwitz criteria<sup>10</sup>:

$$b > 0, \quad (37)$$

$$\bar{\alpha}_1 > 0, \quad (38)$$

$$\bar{\alpha}_2 > 0, \quad (39)$$

$$\bar{\alpha}_4 > 0, \quad (40)$$

$$\bar{\alpha}_1 \bar{\alpha}_2 \bar{\alpha}_3 > \bar{\alpha}_1^2 \bar{\alpha}_4 + \bar{\alpha}_3^2 b. \quad (41)$$

Since all parameters appearing in Eqs. (27)–(36) are nonnegative, conditions (37)–(40) cannot be violated. Therefore the only possible way this system could become unstable is by violating condition (41).

The task of substituting Eqs. (27)–(34) into (41) and rearranging terms is arduous but the result is interesting and useful. Most of the terms on the right-hand side of (41) are cancelled by terms on the left-hand side. The final expression can be grouped into a polynomial of just over 300 terms of which a mere seven are negative. Six of these negative terms are capable of dominating all the remaining terms in the polynomial under the right conditions. The use of only parameters whose physically meaningful range is the positive real axis makes it simple to separate physically meaningless violations of the stability condition from real instabilities.

The terms in stability condition (41) must be carefully arranged in order to simplify the determination of the boundary of stability. First note that the stability condition is a tenth degree polynomial in  $k$ . If the stability condition is written as

$$H(k) > 0, \quad (42)$$

where

$$H(k) = Pk^{10} + Qk^8 + Rk^6 + Sk^4 + Tk^2 + U, \quad (43)$$

then the boundary of stability will occur when the coefficients  $P$ ,  $Q$ ,  $R$ ,  $S$ ,  $T$ , and  $U$  take on values such that the minimum value of  $H(k)$  is zero. The value of  $k$  which does this will be the dimensionless wave vector of the undamped fluctuation  $k_c$ ,

$$H(k_c) = 0. \quad (44)$$

Since there are no backreactions the system comes to equilibrium when  $a$  is zero. Thus increasing  $a$  moves the constraints farther from equilibrium to produce an instability. It is therefore desirable to arrange the coefficients in  $H(k)$  in powers of  $a$  so that their behavior as the system moves away from equilibrium may easily be followed:

$$P = P_0 a + P_1, \quad (45)$$

$$Q = Q_0 a^2 + Q_1 a + Q_2, \quad (46)$$

$$R = R_0 a^3 + R_1 a^2 + R_2 a + R_3, \quad (47)$$

$$S = (S_0 a^3 + S_1 a^2 + S_2 a + S_3) a, \quad (48)$$

$$T = (T_0 a^3 + T_1 a^2 + T_2 a + T_3) a^2, \quad (49)$$

$$U = (U_0 a^3 + U_1 a^2 + U_2 a + U_3) a^3. \quad (50)$$

The expressions for the coefficients which follow have been arranged in powers of  $e$ :

$$P_0 = e^2(1+e)b^2, \quad (51)$$

$$P_1 = bP_0, \quad (52)$$

$$Q_0 = eb + e^2(2b + 3b^2 + 5b^2\gamma + b^3\gamma) + e^3(b + 2b^2 + 3b^2\gamma + b^3\gamma), \quad (53)$$

$$Q_1 = e(2b^2) + e^2(4b^2 + 3b^3 + 5b^3\gamma) + e^3(2b^2 + 2b^3 + 3b^3\gamma), \quad (54)$$

$$Q_2 = eb^3 + e^2(2b^3) + e^3b^3, \quad (55)$$

$$R_0 = e(1 + 3b + 4b\gamma + 2b^2\gamma + 3b^2\gamma d) + e^2(1 + 4b + 3b^2 + 6b\gamma + 12b^2\gamma + 2b^3\gamma + 8b^2\gamma^2 + 3b^2\gamma d + 4b^3\gamma^2) + e^3(b + b^2 + b\gamma + 4b^2\gamma + b^3\gamma + 2b^2\gamma^2 + 2b^3\gamma^2), \quad (56)$$

$$R_1 = b + e(4b + 6b^2 + 8b^2\gamma + 2b^3\gamma + 2b^3\gamma d) + e^2(4b + 8b^2 + 3b^3 + 13b^2\gamma + 12b^3\gamma + 8b^3\gamma^2 + 2b^3\gamma d) + e^3(b + 2b^2 + b^3 + 3b^2\gamma + 4b^3\gamma + 2b^3\gamma^2), \quad (57)$$

$$R_2 = b^2 + e(4b^2 + 3b^3 + 4b^3\gamma) + e^2(4b^2 + 4b^3 + 6b^3\gamma) + e^3(b^2 + b^3 + b^3\gamma), \quad (58)$$

$$R_3 = e(1+e)b^3, \quad (59)$$

$$S_0 = 2b\gamma d - b^2\gamma d + e(2 + 3b + 2\gamma + 10b\gamma + 4b^2\gamma + 5b\gamma^2 + 3b\gamma d + 6b^2\gamma^2 + 4b^2\gamma d + b^3\gamma^2 + 11b^2\gamma^2 d + b^3\gamma^2 d) + e^2(1 + 2b + \gamma + b^2 + 7b\gamma + 7b^2\gamma + 4b\gamma^2 + 2b\gamma d + b^3\gamma + 12b^2\gamma^2 + 2b^2\gamma d + 4b^3\gamma^2 + 4b^2\gamma^3 + 5b^2\gamma^2 d + 4b^3\gamma^3 + b^3\gamma^2 d), \quad (60)$$

$$S_1 = 1 + 3b + 4b\gamma + b^2\gamma + 3b^2\gamma d + e(2 + 8b + 6b^2 + 10b\gamma + 21b^2\gamma + 4b^3\gamma + 10b^2\gamma^2 + 5b^2\gamma d + 6b^3\gamma^2 + 4b^3\gamma d + 7b^3\gamma^2 d) + e^2(1 + 4b + 4b^2 + 6b\gamma + b^3 + 15b^2\gamma + 7b^3\gamma + 10b^2\gamma^2 + 3b^2\gamma d + 12b^3\gamma^2 + 2b^3\gamma d + 4b^3\gamma^3 + 3b^3\gamma^2 d), \quad (61)$$

$$S_2 = 2b + 3b^2 + 4b^2\gamma + b^3\gamma d + e(4b + 8b^2 + 3b^3 + 10b^2\gamma + 10b^3\gamma + 5b^3\gamma^2 + 2b^3\gamma d) + e^2(2b + 4b^2 + 2b^3 + 7b^2\gamma + 4b^3\gamma^2 + b^3\gamma d + 6b^2\gamma^2), \quad (62)$$

$$S_3 = b^2 + e(2b^2 + 2b^3 + 2b^3\gamma) + e^2(b^2 + b^3 + b^3\gamma), \quad (63)$$

$$T_0 = 2\gamma d + 2b\gamma d + 6b\gamma^2 d - 2b^2\gamma^2 d + 2b^2\gamma^2 d^2 - 2b^2\gamma d + e(1 + 2\gamma + b + 6b\gamma + \gamma^2 + 2\gamma d + 2b^2\gamma + 7b\gamma^2 + b\gamma d + 7b^2\gamma^2 + b^2\gamma d + 7b\gamma^2 d + 2b\gamma^3 + b^3\gamma^2 + 4b^2\gamma^3 + 6b^2\gamma^2 d + 2b^3\gamma^3 + b^3\gamma^2 d + 10b^2\gamma^3 d + 2b^2\gamma^2 d^2 + 2b^3\gamma^3 d), \quad (64)$$

$$T_1 = 2 + 3b + 2\gamma + 9b\gamma + 2b^2\gamma + 5b\gamma^2 + 2b\gamma d + 3b^2\gamma^2 + 4b^2\gamma d + 8b^2\gamma^2 d + b^3\gamma^2 d + b^3\gamma^2 d^2 + e(2 + 4b + 2\gamma + 2b^2 + 12b\gamma + 13b^2\gamma + 6b\gamma^2 + 2b\gamma d + 2b^2\gamma + 17b^2\gamma^2 + 3b^2\gamma d + 7b^3\gamma^2 + 2b^3\gamma d + 4b^2\gamma^3 + 10b^2\gamma^2 d + 4b^3\gamma^3 + 7b^3\gamma^2 d + 6b^3\gamma^2 d + 4b^3\gamma^2 d^2), \quad (65)$$

$$T_2 = 1 + 4b + 3b^2 + 5b\gamma + 9b^2\gamma + 5b^2\gamma^2 + 2b^2\gamma d + 2b^3\gamma + 3b^3\gamma^2 d + e(1 + 4b + 4b^2 + 5b\gamma + b^3 + 12b^2\gamma + 6b^3\gamma + 6b^2\gamma^2 + 2b^2\gamma d + 7b^3\gamma^2 + 2b^3\gamma d + 2b^3\gamma^3 + 4b^3\gamma^2 d), \quad (66)$$

$$T_3 = b + 2b^2 + 2b^2\gamma + b^3\gamma d + e(b + 2b^2 + b^3 + 2b^2\gamma + 2b^3\gamma + b^3\gamma^2 + b^3\gamma d), \quad (67)$$

$$U_0 = \gamma d + 2\gamma^2 d - b^2\gamma d + 4b\gamma^2 d - 2b^2\gamma^2 d + 4b\gamma^3 d - 2b^2\gamma^2 d^2 + 2b^2\gamma^2 d^2 + 4b^2\gamma^3 d^2, \quad (68)$$

$$U_1 = 1 + b + 2\gamma + 5b\gamma + \gamma^2 + \gamma d + b^2\gamma + 6b\gamma^2 + 3b^2\gamma^2 + b^2\gamma d + 2b\gamma^3 + 2b\gamma^2 d + 2b^2\gamma^3 + 7b^2\gamma^2 d + b^3\gamma^2 d + 4b^2\gamma^3 d - b^2\gamma^2 d^2 + 2b^3\gamma^3 d + b^3\gamma^2 d^2 + 2b^3\gamma^3 d^2, \quad (69)$$

$$U_2 = 1 + 2b + \gamma + b^2 + 5b\gamma + 5b^2\gamma + 3b\gamma^2 + b\gamma d + 6b^2\gamma^2 + b^2\gamma d + b^3\gamma d + 2b^2\gamma^3 + b^2\gamma^2 d + 4b^3\gamma^2 d + 2b^3\gamma^3 d, \quad (70)$$

$$U_3 = b + b^2 + b\gamma + 2b^2\gamma + b^2\gamma^2 + b^3\gamma d + b^3\gamma^2 d. \quad (71)$$

The seven negative terms are found in the  $e$  independent parts of  $S_0$ ,  $T_0$ ,  $U_0$ , and  $U_1$  and each of these terms is capable of making  $S_0$ ,  $T_0$ ,  $U_0$ , or  $U_1$  negative under appropriate conditions. If  $S_0$ ,  $T_0$ , or  $U_0$  are negative then sufficiently far from equilibrium (large  $a$ )  $S$ ,  $T$  and  $U$  will become negative with the possibility that  $H(k)$  possesses a minimum which is also negative. The strategy adopted here for finding the boundary of stability is first to find the condition on the coefficients  $P$ ,  $Q$ ,  $R$ ,  $S$ ,  $T$ ,  $U$  which makes the minimum of  $H(k)$  zero. Then the signs of  $S_0$ ,  $T_0$ ,  $U_0$  are checked to see if any are negative. If so, increasing  $a$  will make the corresponding  $S$ ,  $T$ , or  $U$  negative. The condition on the coefficients  $P \cdots U$  can then be tested as  $a$  is increased so see if  $H$  can be made zero.

The negative term in  $U_1$  cannot be handled by this technique. This term will make  $U_1$  negative, for example, as  $\delta \rightarrow \infty$  if

$$\begin{aligned} b &\propto \delta^{-1}, \\ \gamma &\propto \delta^{-2}, \\ d &\propto \delta^5. \end{aligned} \quad (72)$$

If  $U_1$  went negative while  $U_0$  remained positive, a local unstable region could occur for a finite range of  $a$ . Such a region would be difficult to locate. It is fortunate that the distribution of the other six negative terms in  $H(k)$  makes the problem of finding the boundary of stability as simple as it is.

#### IV. THE BOUNDARY OF STABILITY

A condition on the coefficients of (43) which will hold at the boundary of stability needs to be derived. Temporarily let us consider the restricted case when  $e=0$ . Then both  $P$  and  $Q$  are zero and  $H(k)$  is a cubic equation in  $k^2$ . This cubic can become negative in two ways. It may be negative in the region of  $k^2=0$  if  $U$  is negative. For this case the boundary of stability occurs when

$$U=0 \quad (73)$$

and the undamped perturbation has a zero wave vector. Secondly, the cubic can become negative by having a local minimum and the boundary of stability occurs when  $H$  is zero at this minimum.

The condition that a cubic has a minimum value of zero will now be stated. First write the cubic in the form

$$U(\xi^3 + 3X\xi^2 + 3Y\xi + 1) = 0, \quad (74)$$

where

$$\begin{aligned} \xi &= (R/U)^{1/3} k^2, \\ X &= S/(3R^{2/3}U^{1/3}), \\ Y &= T/(3R^{1/3}U^{2/3}). \end{aligned}$$

This cubic in  $\xi$  has a minimum at

$$\xi = -X + (X^2 - Y)^{1/2} \quad (75)$$

only when the discriminant is positive,

$$X^2 > Y. \quad (76)$$

For  $H$  to be zero at this minimum the following relation between  $X$  and  $Y$  must hold:

$$4X^3 + 4Y^3 - 3X^2Y^2 - 6XY + 1 = 0. \quad (77)$$

For this minimum to occur for positive  $\xi$  it is also necessary that either  $X$  or  $Y$  or both is negative.

The procedure for determining the value of  $a$  for which the system becomes unstable for given values of  $b$ ,  $\gamma$ ,  $d$  breaks down into the following cases:

- (1)  $S_0$ ,  $T_0$ ;  $U_0 > 0$ . The system is stable.
- (2)  $S_0$ ,  $T_0 > 0$ ;  $U_0 < 0$ . A value of  $a$  satisfying Eq. (73) may always be found. The unstable perturbation has zero wave vector. Since this case produces homogeneous time oscillations, it will be termed a "time instability".
- (3)  $S_0$  and/or  $T_0 < 0$ ;  $U_0 > 0$ . One may make  $S$  and/or  $T$  negative for sufficiently large  $a$ . If an instability exists  $a$  will be larger than the value which first makes  $S$  or  $T$  negative. Call this value  $a^*$ . If (77) can be satisfied for  $a > a^*$  then the system is unstable with a nonzero wave vector for the undamped fluctuation. Otherwise the system is stable. Since in this case the unstable mode is periodic in space, it will be termed a "space instability".
- (4)  $S_0$  and/or  $T_0 < 0$ ;  $U_0 < 0$ . The system will be unstable. To find  $a$ , one must carry out the procedures of Case 2 and Case 3 to see which type of instability occurs first.

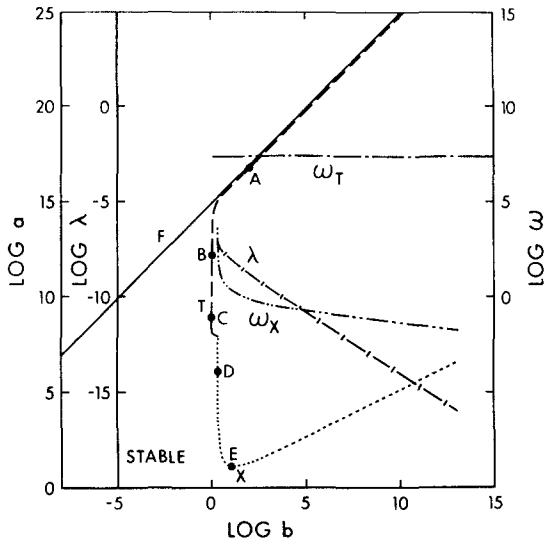


FIG. 2. The boundary of the stable region when  $c=10^{15}$ ,  $d=1$ ,  $e=0$ . The lower left portion is stable as well as areas of the diagram that can be reached from this region without crossing line  $F$  (flip-flop line), line  $T$  (time instability line), or line  $X$  (space instability line). The frequencies of lines  $T$  and  $X$  are lines  $\omega_T$  and  $\omega_X$  and the wavelength of  $X$  is the line labeled  $\lambda$ .  $\lambda=2\pi/k$ . Points A, B, C, D, and E are discussed in the text.

The wave vector of the unstable mode may be determined from Eq. (75) and Eq. (74) once the boundary of stability has been found. A simple formula for the frequency of this mode which applies whether or not the wave vector is zero may be derived by writing the characteristic equation in factored form for the case where one of the roots is pure imaginary,  $i\Omega$ , and another is its complex conjugate. ( $\Omega$  is real but  $\psi$  is complex.)

$$b(\omega - i\Omega)(\omega + i\Omega)(\omega - \psi)(\omega - \psi^*) = 0;$$

multiplying this out and comparing with (26) yields the formula

$$\Omega = (\bar{\alpha}_3/\bar{\alpha}_1)^{1/2}$$

for the frequency of the unstable mode.

## V. METHOD OF COMPUTATION

A computer is well suited to making the large number of systematic decisions required to find the boundary of stability. A logarithmic lattice in  $b\gamma d e$  space was scanned and the sign of  $S_0$ ,  $T_0$ ,  $U_0$  noted. When these polynomials are negative the cubic polynomial in  $a$  for  $S$ ,  $T$ , or  $U$  was solved to determine the values of  $a$  which would make each of these zero. The relative values of these  $a$ 's determine which of cases (1), (2), (3), or (4) occur. The value of  $a$  was increased systematically until the system was or was not found to become unstable. An IBM 360/67 computer was capable of evaluating the stability of hundreds or thousands of points in  $b\gamma d e$  space per second with very little storage required.

A slight complication occurs when  $e \neq 0$ . In this case

$H(k)$  is quintic rather than cubic in  $k^2$  and (77) does not apply. This difficulty was overcome by noting that no new minimum could occur in  $H(k)$  when  $P$  or  $Q$  are positive rather than zero. Temporarily putting  $P=0$  and  $Q=0$  would distort the quintic into a cubic and then Eq. (77) could be used to find the minimum. If the minimum were zero when  $U=0$  the solution would be accurate. If the minimum were zero for non-zero  $k_c$  then the calculation was repeated with  $R$  replaced by

$$R' = Pk_c^4 + Qk_c^2 + R.$$

Usually only one iteration was necessary to check for convergence.

Since  $a$ ,  $b$ , and  $c$  are experimentally variable quantities while  $d$  and  $e$  are not, the best way to represent the results is by giving the boundary surface of stability in  $abc$  space for values of  $d$  and  $e$ . The calculations produced an  $abc$  space surface which appears most interesting when cross sections at constant  $c$  are viewed. The computer was programmed to generate such curves of  $a$  versus  $b$  at constant  $c$ ,  $d$ , and  $e$  from the value of  $a$  at particular values of  $b$ ,  $\gamma$ ,  $d$ , and  $e$ . To do this the desired values of  $b$ ,  $c$ ,  $d$ , were fed into the computer. The critical value of  $a$  was determined for each  $\gamma$  in a scan of  $\gamma$  for each point in a scan of the  $b, d, e$  lattice. From the resulting value of  $a$ , Eq. (15) could be used to calculate  $c$ . After a complete scan of  $\gamma$  was made, the calculated values of  $c$  were compared with the desired values of  $c$  and a new set of  $\gamma$  points were calculated by interpolation. A new scan of  $\gamma$  space was

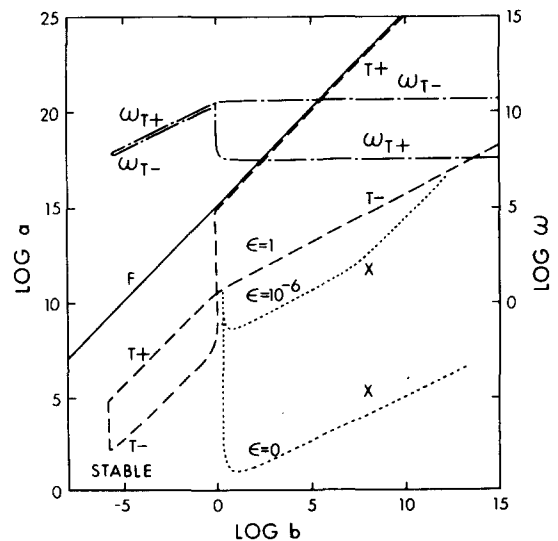


FIG. 3. The boundary of the stable region when  $c=10^{15}$ ,  $d=10^6$ , and  $e$  takes the three values 0,  $10^{-6}$ , and 1. See Fig. 2 for labeling of the lines. The effect of increasing  $e$  is that the lower boundary (marked X) rises to a new position (marked X) and then rises further to reveal a time boundary (marked T). The time boundaries (marked T) are not changed by  $e$ .  $T+$  and  $T-$  label the upper and lower time boundaries with frequencies labeled  $\omega_{T+}$  and  $\omega_{T-}$ .



made using the calculated points and the process was repeated until the values of  $c$  obtained converged to the desired ones. Several difficulties were encountered here which required the programming of various strategies for determining  $c$  into the program. Sometimes there would be a critical value of  $\gamma$  such that the system was stable on one side of  $\gamma_c$  but not on the other. In this case  $a$  becomes infinite and to get the desired value of  $a(c, b)$  one must use Eq. (15) valued at  $\gamma_c$ . Another problem is the occurrence of multiple boundaries of stability for a fixed value of  $b$  and  $c$ . The advantage of first doing the calculation in  $ab\gamma$  space is that no multiple boundaries are encountered. The iteration to the desired  $c$  value must be done carefully so that the new  $\gamma$  is calculated from the right pair of  $a$ 's for a given  $c$  value. Once  $a$  was determined for each desired  $c$  a further step in the scan of  $b$  was made. The data points were then sorted into curves of  $a$  versus  $b$  for constant  $c$  and plotted using a Calcomp plotter.

## VI. RESULTS OF COMPUTATION

The shape of the  $abc$  space surface is quite complicated and changes greatly with  $d$  and  $e$ . In principle a measurement of the shape of this surface would easily determine  $d$  and  $e$  if the reaction kinetics applied. Otherwise the kinetics could be rejected.

A sample of five graphs appears in Figs. 2-7 which illustrates the main features of the boundary of stability and its dependence on  $d$  and  $e$ . In each graph the region of stability is bounded by three types of lines.

(1) Flip-flop line. The line  $a=bc$  divides the region where the reaction is "off" with larger  $a$  from the "on"

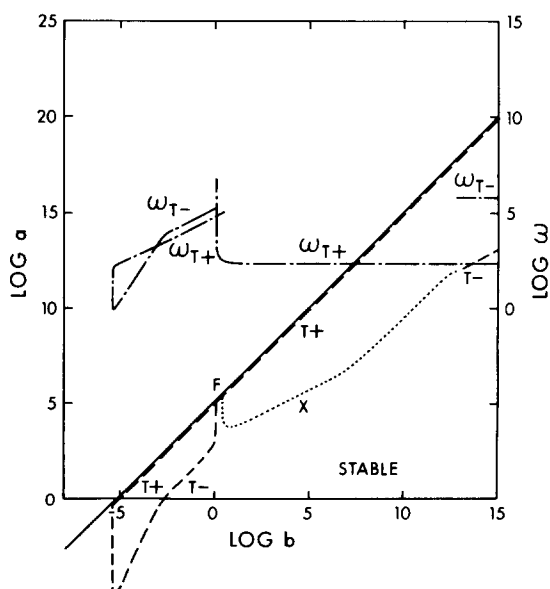


FIG. 4. The boundary of the stable region when  $c=10^5$ ,  $d=10^6$ , and  $e=10^{-8}$ . This cross section of  $abc$  space shows the lowering of line  $F$  to compare with  $c=10^{15}$  in Fig. 3. See Figs. 2 and 3 for labeling of the lines.

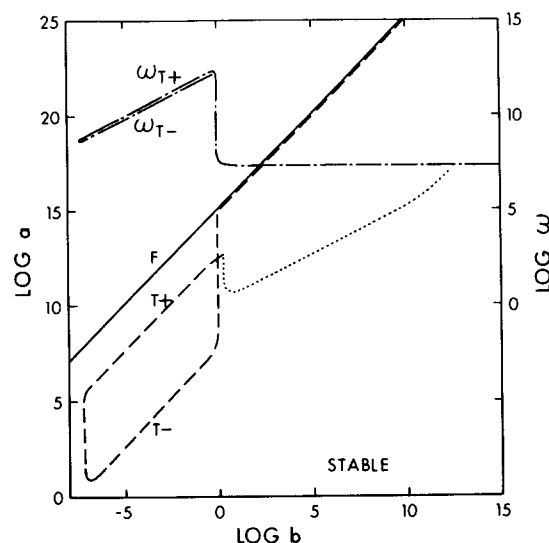


FIG. 5. The boundary of stability when  $c=10^{15}$ ,  $d=10^{10}$ ,  $e=10^{-6}$ . Compare with Figs. 3, 6, and 7 which differ only in  $d$ . See Figs. 2 and 3 for labeling of the lines.

region with smaller  $a$ . This is the solid diagonal line labeled  $F$  in Figs. 2-7.

(2) Time instability line. The unstable perturbation has zero wave vector and the system oscillates homogeneously. This line is marked  $T$  in Figs. 2-7. If a peninsula of instability occurs, the lower edge of the peninsula is marked  $T-$  and the upper edge  $T+$ .

(3) Space instability line. The unstable perturbation has a nonzero wave vector. The wavelength,  $\lambda=2\pi/k$ , of this wave vector is shown on Fig. 2 as a dashed line but was not calculated for the other cases. Space instability lines are marked by  $X$ .

For boundaries of types (2) and (3) the frequency of the unstable mode has been shown on some of the graphs and is labeled  $\omega_X$  or  $\omega_T$ .

Figure 2 is a stability diagram for the parameter values  $c=10^{15}$ ,  $d=1$ ,  $e=0$ . The stable region is the lower portion of the diagram. For  $b<1$  the system is stable up to the flip-flop line. For  $b>1$  a peninsula of instability extends into the diagram from the upper right. At the upper edge of this peninsula is an infinite sliver of stability bounded below by a time instability line and above by the flip-flop line. The frequency of the time line is marked  $\omega_T$ . The lower edge of the peninsula is a space instability line with frequency  $\omega_X$  and wavelength  $\lambda$ . Note that the frequency of the space instability line is approximately eight orders of magnitude less than for the upper time instability line. The wavelength also varies inversely with  $b$ . With such great variation in frequency and wavelength possible an unstable system could easily go unnoticed if the frequencies and wavelengths were not in a conveniently observable range.

In Fig. 3, three stability diagrams for  $e=0$ ,  $10^{-6}$ , and 1 are superposed. When  $e$  is increased  $V$  is able to

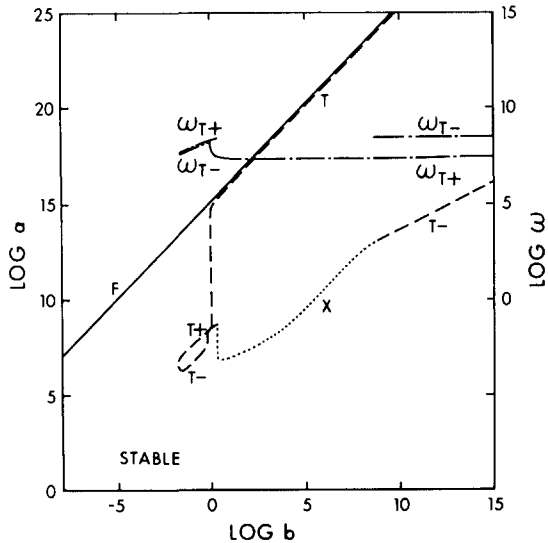


FIG. 6. The boundary of stability when  $c=10^{15}$ ,  $d=10^2$ ,  $e=10^{-6}$ . See Figs. 2 and 3 for labeling of the lines.

diffuse in comparison with  $Y$  and the space instability is gradually eliminated. This occurs because the  $e$  terms in  $S$  and  $T$  are all positive. The lines  $T$  and  $F$  are independent of  $e$  because  $U$  is. For large enough  $e$  the space instability line has risen high enough to reveal the line  $T-$ . This diagram for the  $e=1$  case is what one would obtain if diffusion had been omitted from the problem originally. Adding diffusion destabilizes a region of the diagram which would otherwise be stable. However, as observed here, adding a second diffusing species may stabilize a portion of the diagram destabilized by another diffusing species but not a region which is time unstable.

Figure 4 and the  $e=10^{-6}$  diagram of Fig. 3 show two different cross sections of  $abc$  space for different values of  $c$ . As  $c$  increases the flip-flop line drops down faster than the curves below it. Distortions appear in the time island but the curves marked  $X$  and  $T-$  move downward without distortion. This downward movement of  $X$  and  $T-$  does not occur in the case when  $e=0$  where the space instability line  $X$  is independent of  $c$ . When  $c$  becomes  $10^{-5}$  most of the interesting features of these diagrams have disappeared. For smaller  $c$  the peninsula of instability is a wedge (time only). The diagrams have been drawn for  $c=10^{15}$  so that full details of their structure may be seen before it is absorbed by the descent of the flip-flop line.

The remaining Figs. 5, 6, and 7 compare this case  $c=10^{15}$ ,  $e=10^{-6}$  at different values of  $d$ . Compare these also with Fig. 3. At large  $d$  ( $d=10^{10}$ ) the time island is large and a characteristic distortion at its tip, which does not occur for the  $d=10^6$  case until the flip-flop line has descended partly, would be more pronounced if  $d$  were larger yet. When  $d=10^2$  the time island has become small and the space instability line has narrowed. When  $d<1$  a widening of the lower part of the

sliver of stability occurs as illustrated for the  $d=10^{-6}$  case in Fig. 7. The great effect that the parameter  $d=k_3/k_1$  has on these diagrams would make it possible to determine  $d$  from measurements of the boundary of stability.

The graphs give sufficient information to determine which negative term in  $H(k)$  is responsible for cancelling out all the positive terms. The term  $-b^2\gamma d$  in  $U_0$  is dominant along the sliver of stability near the flip-flop line and along the vertical part of the peninsula of instability. The term  $-2b\gamma^2d^2$  produces the island of time instability for  $b<1$  while the vertical part of the space instability is produced by the factor  $2-b$  in  $S_0$ . With careful reasoning the major features of the graphs could be determined analytically by considering when each negative term could be dominant.

## VII. THE NORMAL MODES

The amplitudes and phases of the undamped perturbation of  $V$ ,  $W$ ,  $X$ ,  $Y$ , and  $Z$  can be obtained from the eigenvectors of the matrix  $M$ . An independent program was used to calculate these eigenvectors and their eigenvalues at selected points on the boundary of stability. The resulting values of  $\omega$  confirmed the location of the boundary and the frequencies obtained previously.

The eigenvectors at the points marked  $A$ ,  $B$ ,  $C$ ,  $D$ , and  $E$  in Fig. 2 are tabulated in Table I. They give the relative values of  $V$ ,  $W$ ,  $Y$ , and  $Z$  and have been normalized with the largest of these set to one. Since only perturbations with uniform  $C$  were considered,

$$\Delta X = -\Delta Y - \Delta Z.$$

For comparison the relative values of the concentrations of the steady state, normalized in the same manner, are also given in the table.

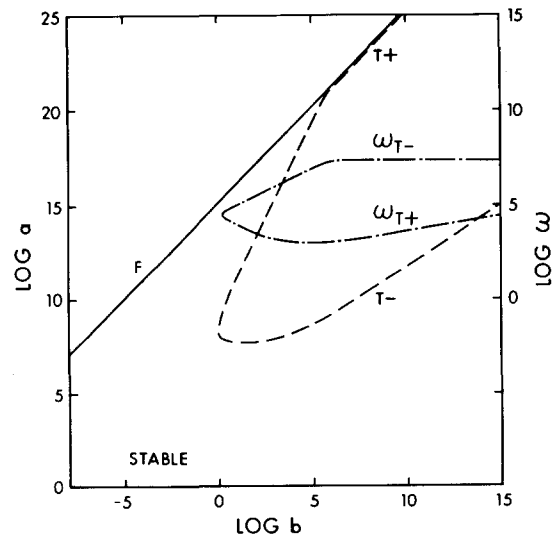


FIG. 7. The boundary of stability when  $c=10^{15}$ ,  $d=10^{-6}$ ,  $e=10^{-6}$ . See Figs. 2 and 3 for labeling of the lines.

TABLE I. Steady states, eigenvectors, and phases for points from Fig. 2.

Point		V	W	X	Y	Z
A	$v_0^a$	$1.0 \times 10^{-19}$	$1.0 \times 10^{-17}$	$1.0 \times 10^{-17}$	1.0	1.0
	$ \Delta v ^b$	$4.6 \times 10^{-12}$	$4.6 \times 10^{-10}$	$\sim 0$	1.0	1.0
	phase <sup>c</sup>	0	0	0	1.0	0
B	$v_0$	$4.3 \times 10^{-13}$	$4.4 \times 10^{-13}$	$4.4 \times 10^{-13}$	$2.3 \times 10^{-3}$	1.0
	$ \Delta v $	$9.5 \times 10^{-15}$	$3.7 \times 10^{-10}$	$\sim 0$	1.0	1.0
	phase	1.0	0	0	1.0	0
C	$v_0$	$1.1 \times 10^{-9}$	$1.1 \times 10^{-9}$	$1.7 \times 10^{-9}$	$9.3 \times 10^{-7}$	1.0
	$ \Delta v $	$1.2 \times 10^{-3}$	$1.2 \times 10^{-3}$	$\sim 0$	1.0	1.0
	phase	0.97	-0.03	0	1.0	0
D	$v_0$	$8.3 \times 10^{-7}$	$1.7 \times 10^{-6}$	$8.4 \times 10^{-7}$	$6.0 \times 10^{-10}$	1.0
	$ \Delta v $	$7.5 \times 10^{-4}$	$7.5 \times 10^{-4}$	1.0	$2.7 \times 10^{-7}$	1.0
	phase	0.98	-0.04	1.0	1.0	0
E	$v_0$	$8.2 \times 10^{-2}$	0.82	$8.1 \times 10^{-2}$	$1.3 \times 10^{-15}$	1.0
	$ \Delta v $	$5.9 \times 10^{-2}$	1.0	0.18	$5.4 \times 10^{-16}$	0.18
	phase	0.19	0	0.70	1.0	-0.30

<sup>a</sup> Normalized with the largest of  $V_0$ ,  $W_0$ ,  $Y_0$ ,  $Z_0$  equal to one.

<sup>b</sup> Normalized with the largest of  $\Delta V_0$ ,  $\Delta W_0$ ,  $\Delta Y_0$ ,  $\Delta Z_0$  equal to one.

<sup>c</sup> Phases in units of  $\pi$  relative to largest amplitude component. Phases are rounded off to  $\pm 0.01$ .

The unstable mode at the time instability boundary (point A in Fig. 2) is an exchange of C between the two forms Y and Z keeping other concentrations essentially fixed. An increase in Y speeds Reaction (2) producing V, W, and Z which depletes Y by Reaction (4). Comparison with the steady state concentrations reveals that the growth of this mode would be limited eventually by large fractional changes in V and W.

In contrast, the space instability has a very small amplitude variation of Y and the catalyst is exchanged primarily between X and Z. However, the mathematics shows that Y is essential for the instability of the space boundary. As well, the amplitude of  $\Delta V$  is not insignificant and W sometimes has the largest amplitude of all components. Thus, a physical picture of this oscillation must take into account all five concentrations, no two of which are in phase at point E in Fig. 2.

A qualitative description of the space instability at point E will now be given. (See Fig. 8.) Since the concentrations with the larger phases are shifted to occur earlier in time we see that the peak concentration of V is followed soon after by a peak in W and then Z. Shortly after the peak in V the minimum of Y is reached. It is this low value of Y which starts autocatalytic Reaction (2) slowing down in spite of large feedback (V). The minimum of V slows Reaction (4) directly as well as through V and W causing Z to peak soon after. Following this, Reaction (5) is rapidly producing Y which is converted into X by Reaction (2) with only a slight increase in Y. Note that Reactions (2) and (5) are converting the fluctuating component of catalyst from Z to X at a time when Reaction (2) is slowing down

and Y is growing. Thus Y appears to be out of phase with Reactions (2) and (4). Decreasing V and W slows Reactions (2) and (4) when Y is increasing; increasing V and W increases these reactions when Y is decreasing. This is the key to the space instability. If neighboring regions are out of phase the diffusion of Y into a region where it has low concentration helps speed up Reactions (2) and (4) by neutralizing part of the stabilizing out of phase oscillation of Y. This locally external source of Y drives the oscillation making the system unstable when it appears with proper phase.

It should be now clear why the diffusion of V is stabilizing. V is in phase with Reaction (2) and its loss would weaken the acceleration of this reaction. The discussion in this section applies only near the boundary of stability where the linearization of the equations of motion for the perturbation is valid.

## VIII. CONCLUSION

The stability calculation of this system has been enormously complicated by including diffusion into the picture. Without diffusion the coefficients of the characteristic equation Eq. (26),  $\bar{\alpha}_i$ , would be equal to  $\alpha_i$  and the Routh-Hurwitz criteria Eq. (43) would become

$$U > 0,$$

which has only 1/6 the number of terms dealt with here. Furthermore, the difficulty of using Eq. (77) to determine when the minimum of  $H(k)$  was zero would be eliminated along with the problems of iterating to get the minimum of the quintic equation  $H(k)$ .

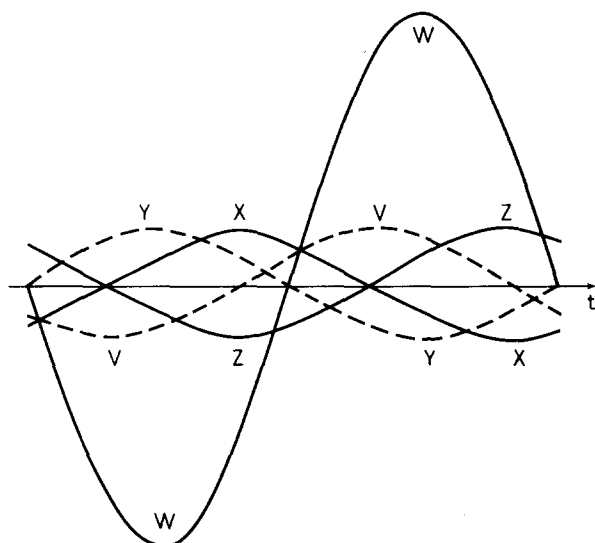


FIG. 8. Amplitude and phase relationships for the undamped perturbation at point *E* in Fig. 2. The amplitude of curves for *V* and *Y* has been greatly increased and *W* has been slightly reduced for clarity.

How much more complicated would this calculation have been if there had been one more reaction intermediate, one more reaction in the model, or one more particle with diffusion? Another reaction intermediate would have made the characteristic equation quintic. Then, instead of just one complicated Routh-Hurwitz criterion (in addition to three trivial ones) there would be a second nontrivial criterion which would be even more complex than the one dealt with here. The terms in this new condition would be fourth degree in the  $\bar{\alpha}_i$ 's. Another reaction would not cause much additional complication except that another parameter in the

determinant Eq. (22) would increase the number of terms in the  $\bar{\alpha}_i$ 's by 25% and  $H(k)$  would have  $(5/4)^3$  as many terms (roughly double). Another particle diffusing would have added a parameter  $e'k^2$  to Eq. (22) which would produce a  $k^6$  term in  $\bar{\alpha}_4$  and  $\bar{\alpha}_3$  but only  $k^4$  in  $\bar{\alpha}_2$  and  $k^2$  in  $\bar{\alpha}_1$ . Although Eq. (41) would then contain a  $k^{12}$  term, one might still be able to treat  $H(k)$  as a cubic and iterate.

The Noyes-Field-Körös mechanism for the bromate-cerium-malonic acid system involves the seven intermediates  $\text{Br}^-$ ,  $\text{HOBr}$ ,  $\text{HBrO}_2$ ,  $\text{BrO}_2^\cdot$ ,  $\text{Ce}^{4+}$ ,  $\text{BrCH}(\text{COOH})_2$ , and  $\text{Br}_2$  as well as the three constraints: total cerium,  $\text{BrO}_3^-$ , and  $\text{CH}_2(\text{COOH})_2$ . Then  $M$  would be a seventh order matrix and the Routh-Hurwitz conditions for its seventh degree characteristic polynomial would be extremely complex. There would be eight Routh-Hurwitz inequalities, four of which would be much more complicated than Eq. (43). The most complex of these would contain 1600 terms which would be 13th order in the  $\bar{\alpha}_i$ 's. A simple calculation shows that  $H_8(k)$  would be 64th order in  $k$  if the diffusion of all species were included.

For the present model the computer time required to calculate the boundary of stability was roughly two orders of magnitude faster than by repeated solution of the eigenvalue problem by the most efficient methods available. If better methods than the Routh-Hurwitz criteria cannot be found the prospects for solving the stability of large reaction systems are not hopeful.

## ACKNOWLEDGMENTS

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<sup>1</sup>P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure Stability and Fluctuations* (Wiley-Interscience, London, 1971).

<sup>2</sup>R. J. Field, E. Körös, and R. M. Noyes, *J. Am. Chem. Soc.* **94**, 8649 (1972).

<sup>3</sup>I. Matsuzaki, J. H. Woodson, and H. A. Liebhafski, *Bull. Chem. Soc. Jap.* **43**, 3317 (1970).

<sup>4</sup>I. Prigogine, R. Lefever, A. Goldbeter, M. Herschkowitz-Kaufman, *Nature (Lond.)* **223**, 913 (1969).

<sup>5</sup>Reference 1, pp. 245, 246.

<sup>6</sup>R. M. Noyes, R. J. Field, and E. Körös, *J. Am. Chem. Soc.* **94**, 1394 (1972).

<sup>7</sup>R. J. Field and R. M. Noyes, *Nature (Lond.)* **237**, 390 (1972).

<sup>8</sup>The stability of the other steady states of this system is simple to calculate. The steady state with  $V = 0$  and general  $Y$  is stable only when  $Y = 0$  and the steady state with general  $V$  and  $Y = 0$  is always stable. These steady states are possible only when  $A = 0$ . If  $C = 0$  a steady state with  $V = Y = 0$  is possible which is stable.

<sup>9</sup>The steady state with  $a > bc$  when all reactions have stopped is easily shown to be stable.

<sup>10</sup>J. L. Willems, *Stability Theory of Dynamical Systems* (Nelson, London, 1970), p. 66.