

Interrupted separatrix excitability in a chemical system

William D. McCormick, Zoltan Noszticzius,^{a)} and Harry L. Swinney
Center for Nonlinear Dynamics and the Department of Physics, The University of Texas, Austin,
Texas 78712

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Models of excitability fall into two broad categories: one with a sharp threshold, the other with a narrow but finite threshold region. In an attempt to clarify the notion, we have studied the application of two models of excitability to experiments on a variant of the Belousov–Zhabotinskii reaction in a well-stirred reactor. An interrupted separatrix model, which has a sharp threshold, is found to describe our experimental results better than a simple nullcline model, which has a finite threshold region.

I. INTRODUCTION

A. Chemical waves and excitability

Chemical waves are most often studied for media that exhibit local (uncoupled) excitable dynamics.^{1,2} But what is the proper definition of excitability for a dynamical system? There is no widely accepted answer to this question. Even for the special case of chemical systems, only qualitative or restricted definitions have been given. Winfree,^{1(a)} a recognized authority in this area, writes “The idea seems clear: a reaction is excitable if it has a unique steady state that the system will approach from all initial conditions, but there exists a locus of initial conditions near which either of two quite different paths may be taken toward the unique steady state. If one of these paths is a lot longer than the other, then the system is ‘excitable.’ But no one has yet offered an exact definition: only examples. As more and more examples have come under study it has become apparent that there are different degrees and kinds of excitability.”

We will discuss two models of excitability and compare the predictions of these models with the behavior of a particular chemical system displaying excitability.

B. Phase portrait with an exact threshold of excitability: The “interrupted separatrix” model

For simplicity we first consider cases where the important dynamics can be captured in a two-dimensional phase portrait. Also, we shall accept Winfree’s stipulation that an excitable dynamical system has an attractive fixed point that is a globally stable steady state. Thus for now we exclude systems displaying limit cycle oscillations.

A phase portrait for the interrupted separatrix model considered by Noszticzius *et al.*³ is depicted in Fig. 1. There are three fixed points: a stable node, a saddle point, and an unstable focus or node. There are two special trajectories which end in the saddle point: they are the separatrices. Separatrices often separate basins of attraction of different attractors, but here we have only one attractor, the stable node, and the whole phase plane serves as its basin of attraction. In this case the separatrices cannot cut the phase plane into two parts—thereby creating bistability—because one

separatrix is interrupted by the unstable focus (or node). Thus the system always returns to its unique asymptotic state, regardless of the initial conditions. On the other hand, if the system is perturbed away from its asymptotic state, the response will be qualitatively different above and below a well-defined “threshold of excitability,” as indicated in Fig. 1(b). The initial conditions leading to qualitatively different trajectories can be arbitrarily close to one another, as long as these initial points are on the opposite sides of the separatrix.

C. Phase portrait with a threshold region of excitability: The simple nullcline model

A picture of excitability discussed by Tyson and Fife⁴ is used much more frequently in the chemical literature than the interrupted separatrix model (e.g., see Refs. 4–11). The phase portrait for this type of excitability can be characterized by its nullclines. For a two-dimensional system

$$\dot{x} = f(x,y),$$

$$\dot{y} = g(x,y),$$

the nullclines are the two curves $f(x,y) = 0$ and $g(x,y) = 0$. In this model one of the nullclines is a nonmonotonic curve with one maximum and one minimum. The other nullcline can be an arbitrary curve, the only limitation being that the two nullclines should have only one intersection, which is the unique fixed point of the system. This fixed point can be stable or unstable according to the value of a system parameter, and it loses stability via a Hopf bifurcation that may be super- or subcritical. When the fixed point is unstable, the system executes limit cycle oscillations; when the fixed point is stable, the system can show excitability. Bistability between the stable steady state and limit cycle oscillations can occur in the neighborhood of a subcritical Hopf bifurcation. This type of excitability is qualitatively different from that occurring in the interrupted separatrix model because the nullcline model has a threshold *region of excitability* instead of a sharp threshold. The width of that region, however, can be very small—the nullcline model contains a small parameter that can be related to the width of the threshold region. To illustrate these properties we will consider the following simple model of excitability studied by Meron and Pelcé (see Fig. 2):¹¹

^{a)} Permanent address: Institute of Physics, Technical University of Budapest, H-1521 Budapest, Hungary.

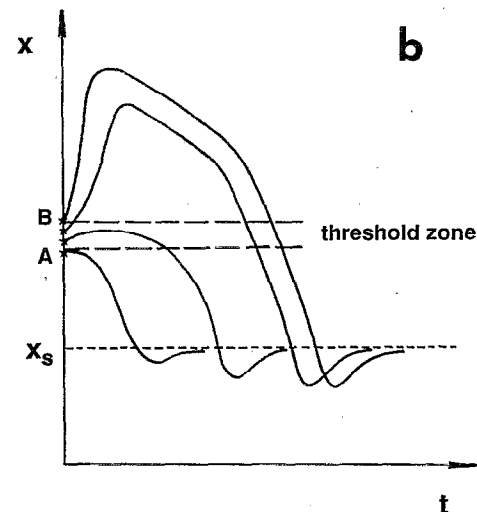
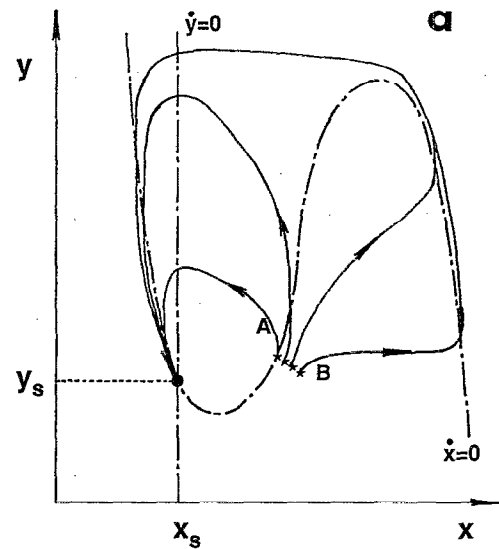
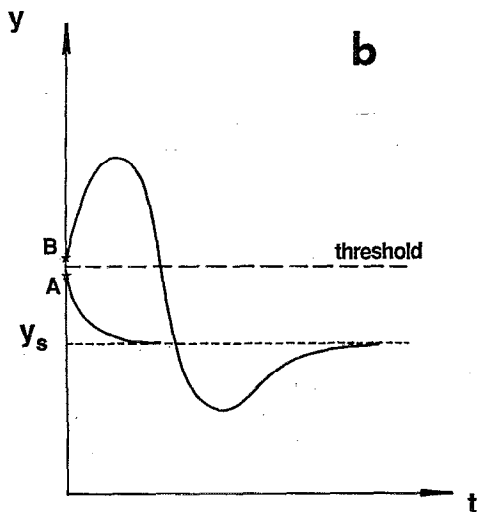
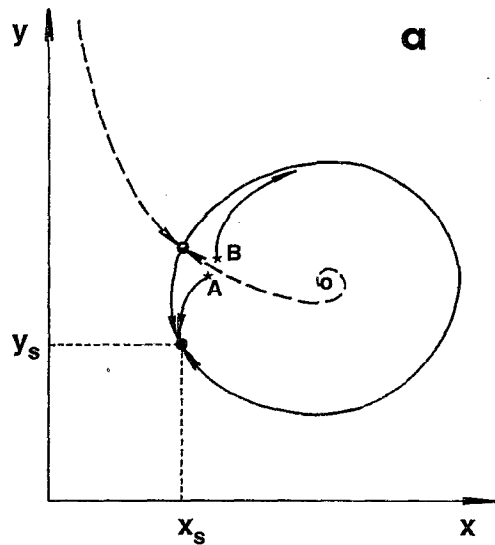


FIG. 1. (a) Phase portrait and (b) time series showing excitability in the interrupted separatrix model. All trajectories (solid lines) in the phase portrait run eventually into the stable node (x_s, y_s) , except the two separatrices (dashed lines), which run into the saddle point. One separatrix starts from an unstable focus or node. Trajectories starting from points A and B on opposite sides of the separatrix follow qualitatively different pathways, as shown in (a), and have a qualitatively different time evolution, as shown in (b).

$$\begin{aligned}\epsilon \dot{x} &= -y + 3x - x^3, \\ \dot{y} &= x - \delta,\end{aligned}$$

where ϵ is a small parameter and δ is another parameter which determines the position and stability of the fixed point. The coordinates of the fixed point are

$$\begin{aligned}x_s &= \delta, \\ y_s &= \delta(3 - \delta^2).\end{aligned}$$

As δ is increased, the position of the nullcline $\dot{y} = 0$ (which is a vertical line in this simple case) and the position of the fixed point are shifted toward increasing x values. A Hopf bifurcation occurs at $\delta = -1$ where there is a transition

FIG. 2. (a) Phase portrait and (b) time series showing excitability in the nullcline picture. All phase space trajectories (solid lines) run eventually into the stable node (x_s, y_s) , which is the only fixed point of the system. This point is also the intersection point of the nullclines ($\dot{x} = 0$, dashed-dotted lines). The $\dot{x} = 0$ nullcline has a minimum and a maximum. The other nullcline can be arbitrary, but only one intersection of the two nullclines is allowed in this picture of excitability, and the point of intersection should be outside of the region between the minimum and the maximum of the $\dot{x} = 0$ nullcline. For the sake of simplicity, the $\dot{y} = 0$ nullcline here is a vertical line, as in the model of Meron and Pelcé. Trajectories starting from A and B are qualitatively different, but now there is a continuous transition between the two, and the time series show a threshold zone rather than a sharp threshold.

from a stable to an unstable focus and then again at $\delta = +1$ where there is a transition from an unstable focus to a stable one. These transitions are independent of ϵ , but ϵ determines the width of the parameter region within which the fixed point is a (stable or unstable) focus. In the simple nullcline picture of excitability, the fixed point is a focus in only two relatively small parameter intervals in the neighborhood of the Hopf bifurcations. For example, in the model of Meron and Pelcé the fixed point is a focus only in the following two small parameter regions

$$-(1 + 2\epsilon^{1/2}/3)^{1/2} < \delta < -(1 - 2\epsilon^{1/2}/3)^{1/2},$$

$$(1 - 2\epsilon^{1/2}/3)^{1/2} < \delta < (1 + 2\epsilon^{1/2}/3)^{1/2}.$$

Between these two small intervals the fixed point is an unstable node; outside these intervals the fixed point is a stable node. It is clear that if ϵ is very small, the parameter interval within which the focus and the Hopf bifurcation can be observed will also be extremely small and may be experimentally unobservable. In this case only a stable node or an unstable node surrounded by a stable limit cycle would be observed; the Hopf bifurcation would occur in a parameter region too narrow to resolve.

The width of the excitability threshold region is also related to ϵ . For example, consider the region between the nullcline $\dot{x} = 0$ and the isocline $\dot{y}/\dot{x} = 1$, where the isocline is given by

$$y = 3x - x^3 - \epsilon(x - \delta).$$

This is the same equation as for the nullcline except for the term $-\epsilon(x - \delta)$. Thus the nullcline and the isocline $\dot{y}/\dot{x} = 1$ (or any other isocline) can be arbitrarily close to each other if ϵ is small enough, i.e., the threshold region can be arbitrarily narrow, depending on ϵ . For sufficiently small ϵ , the width of the threshold region will be smaller than the resolution or noise in the experiments, in which case the threshold will appear to be sharp.

D. Experimental identification of the different types of excitability

We have described two qualitatively different kinds of phase portraits for excitable dynamic systems. (These are very simple models, of course, and some real excitable systems certainly display more complex behavior.) To decide which model provides a better description of the dynamics, a phase portrait should be generated for a series of perturbations of different magnitudes. The results may reveal the existence of a finite threshold region, indicating that a simple nullcline picture is appropriate. On the other hand, the experiments may yield a sharp threshold, indicating that an interrupted separatrix model is the better description. However, in the latter case there may be some uncertainty because a narrow threshold region for excitability can be experimentally indistinguishable from a sharp threshold. Thus additional experimental evidence besides the sharp threshold of excitability is needed to support the interrupted separatrix model as a valid description. If the existence of the two additional fixed points, the saddle point and the unstable focus or node, could be demonstrated, it would constitute strong evidence for the interrupted separatrix model, since these unstable fixed points are absent from the nullcline picture.

To find unstable steady states is not an easy task, but they can be revealed by perturbations that drive the system into the neighborhood of an unstable steady state. Trajectories starting from the neighborhood of the unstable steady state can indicate the existence of such points.¹² Another possibility would be to stabilize the unstable fixed points by some type of feedback.¹³ A third possibility is that by changing a parameter bifurcations can be observed that reveal the

existence of unstable steady states. For example, a saddle-node bifurcation indicates the presence of a saddle, and a Hopf bifurcation assures the existence of an unstable focus, at least in a parameter range near the Hopf bifurcation. This procedure can establish the existence of the unstable fixed points for parameter values not too far from the bifurcation point. (Not too far means that no other bifurcation occurs in this parameter region.) Even though the position of these fixed points in the phase plane and their other properties at the original parameter value cannot be determined by this technique, enough information may be available to choose between the two different pictures of excitability. If the existence of a saddle point and an unstable fixed point in addition to the stable one could be proven, this would support the interrupted separatrix model, while the absence of these points would indicate that the nullcline picture is more appropriate. We now apply these ideas to an excitable chemical system.

II. EXPERIMENTAL

A. Reactor

Some recent experiments on chemical waves^{14,15} have been done in continuously fed unstirred reactors (CFURs). One CFUR design consists of a thin disc of gel, fed continuously by diffusion from a CSTR (continuous flow stirred tank reactor). When the components of the classical Belousov-Zhabotinskii reaction were introduced into the CSTR, Tam *et al.*¹⁵ and Skinner and Swinney¹⁶ found that chemical waves in the diffusively coupled CFUR could be maintained indefinitely. The present study used the same parameter values as in the CFUR experiments,^{15,16} but the design of the reactor was somewhat different, very similar to that of Coffman *et al.*¹⁷ The pumping rate for each of the three feed lines was 0.362 mL/min, giving a residence time in the 11.55 mL reactor of 10.6 min, as in the experiments of Tam *et al.* The feed stream concentrations were as follows: (A) $[\text{KBrO}_3] = 0.09 \text{ M}$, (B) $[\text{malonic acid}] = 0.15 \text{ M}$ and $[\text{ferroin}] = 0.0075 \text{ M}$, and (C) $[\text{H}_2\text{SO}_4] = 0.6 \text{ M}$. Solutions A, B, and C were pumped into the reactor at equal rates; thus without reaction the reactor concentrations would have been $[\text{BrO}_3^-]_0 = 0.03 \text{ M}$, $[\text{malonic acid}]_0 = 0.05 \text{ M}$, $[\text{ferroin}]_0 = 0.0025 \text{ M}$, and $[\text{H}_2\text{SO}_4]_0 = 0.2 \text{ M}$. The reactor was immersed in a thermostated bath at 23 °C. Our system was oscillatory, as expected, since the bromate concentration, 0.03 M, was in the middle of the range in which Tam *et al.* observed oscillations, $0.02 \text{ M} < [\text{BrO}_3^-] < 0.04 \text{ M}$ (reactor concentrations). Oscillations were monitored with a bromide selective electrode (Orion 94-35A). The reference electrode was a double junction Ag/AgCl (Sensorex). Electrode potentials were recorded in a computer at 0.5 s intervals.

B. Chemistry

Bromide and formaldehyde, used as bifurcation parameters, were added to solution C, which also contained 0.6 M H_2SO_4 . Perturbations were accomplished by injecting different amounts and concentrations of NaBrO_2 and NaBr

solutions *directly* into the reactor with a microsyringe (50 μL total volume).

KBrO_3 (Baker) was recrystallized twice from hot water. Malonic acid (Eastern) was recrystallized three times, first from acetone-chloroform, then from ethylacetate, and finally from acetone-chloroform, as described in Ref. 18. Ferroin was prepared from iron(II)-ammonium sulfate (Baker) and phenanthroline (Sigma). $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was used instead of the more common $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to ensure better reproducibility. Results with iron(II)-sulfate were scattered when the system

was near the saddle-node bifurcation point. This was due the partial oxidation of iron(II)-sulfate crystals by air,¹⁹ which slowly decreases the Fe^{2+} content of the iron(II)-sulfate. Solution B was prepared by dissolving malonic acid, iron(II)-ammonium sulfate and phenanthroline together. Phenanthroline was used in slight excess, 0.001 M in addition to the stoichiometric 0.0235 M phenanthroline that was added to 0.0075 M iron(II). Thus dissociation of ferroin was negligible and better reproducibility was achieved. The NaBrO_2 solutions used for perturbation experiments were prepared as in Ref. 20.

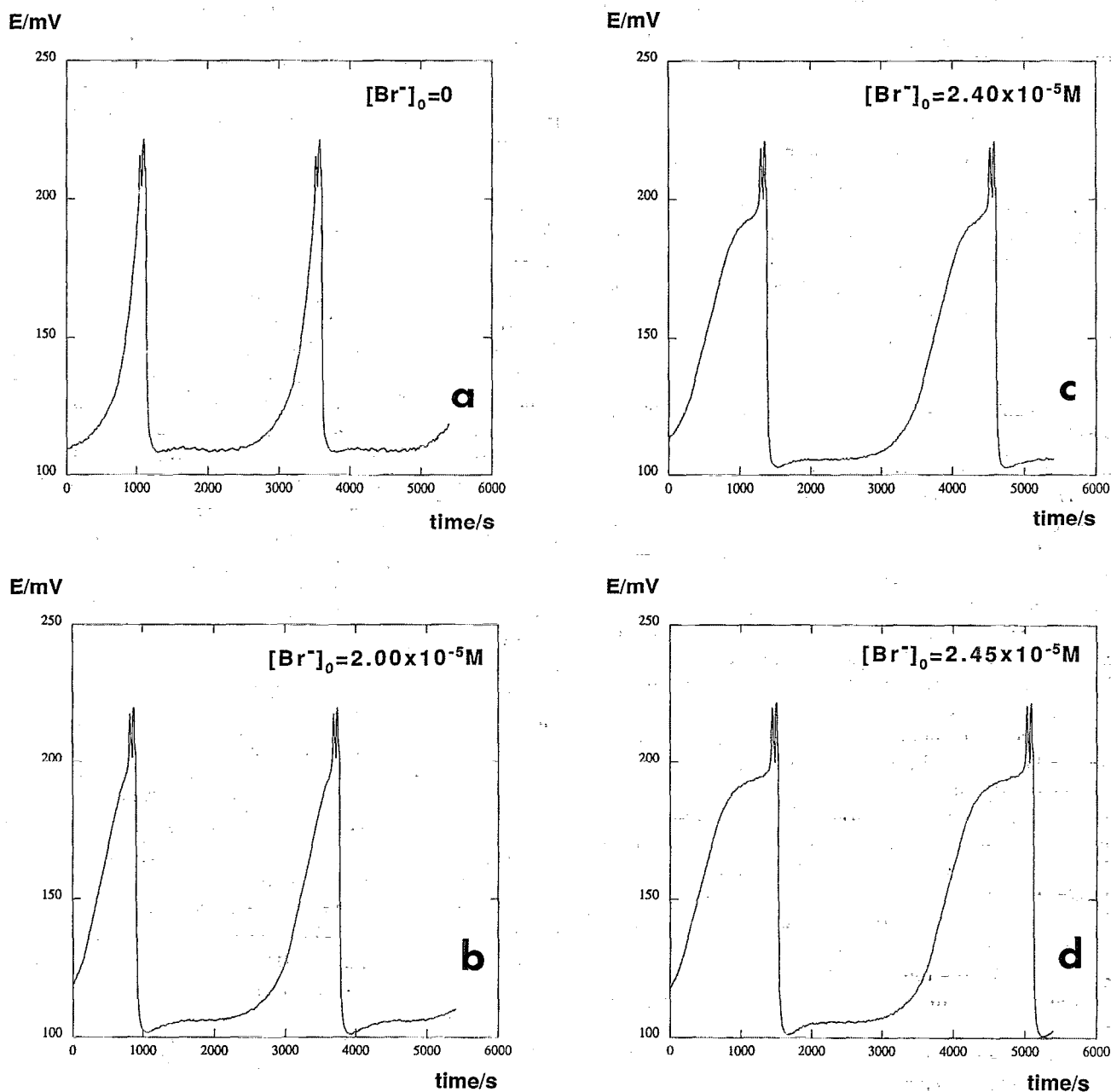
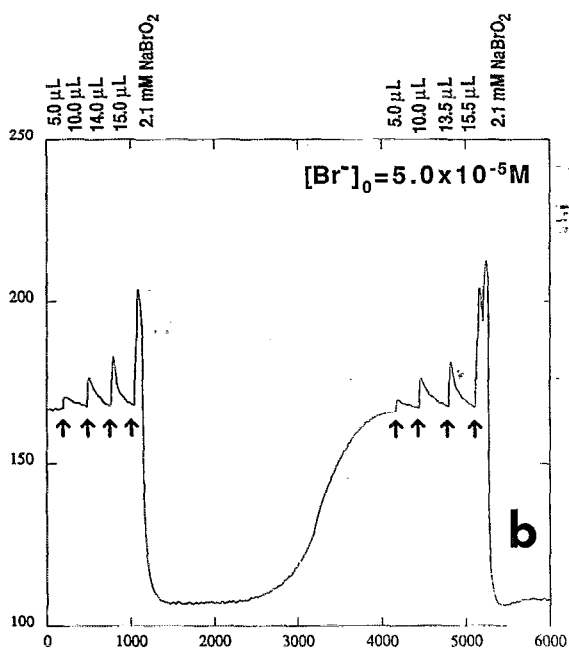
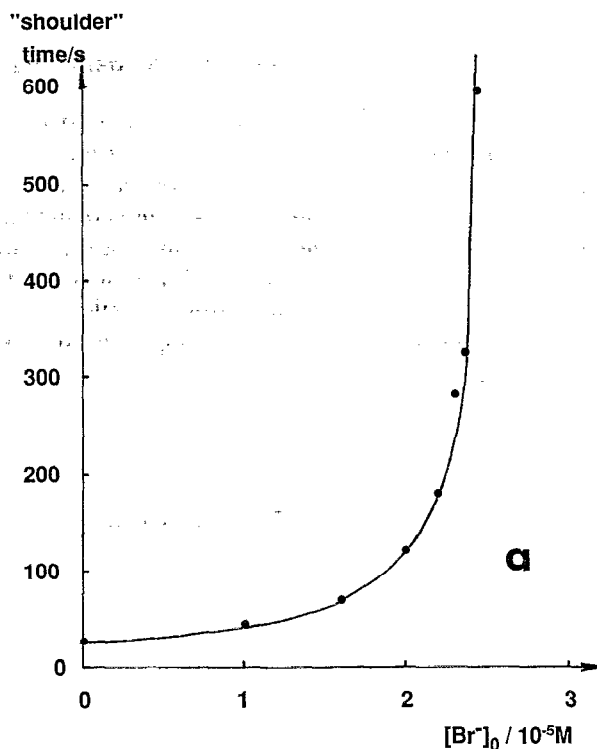
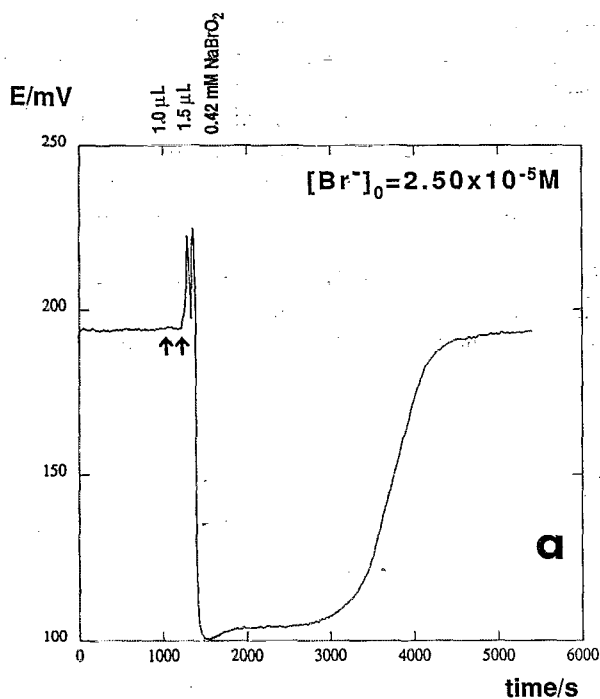


FIG. 3. Evolution of limit cycle oscillations toward excitability in a real chemical system. The control parameter was the bromide concentration $[\text{Br}^-]_0$ (the given concentration is that which would be established after mixing of the three feedstreams together without any reaction). The double peak does not indicate the recurrence of the same state: The intensive blue color of the ferroin appears only after the second peak. A characteristic shoulder develops and grows as the bifurcation point is approached. No periodic state was found for $[\text{Br}^-]_0 > 2.50 \times 10^{-5} \text{ M}$ (see Fig. 4) and no stable steady state was found for $[\text{Br}^-]_0 < 2.45 \times 10^{-5} \text{ M}$. Experiments with perturbations revealed no bistability in the interval of $2.45 \times 10^{-5} \text{ M} < [\text{Br}^-]_0 < 2.50 \times 10^{-5} \text{ M}$, but the exact position of the bifurcation point depended somewhat on the history of the reactor.



perturbation threshold
[NaBrO₂] / 10⁻⁶M

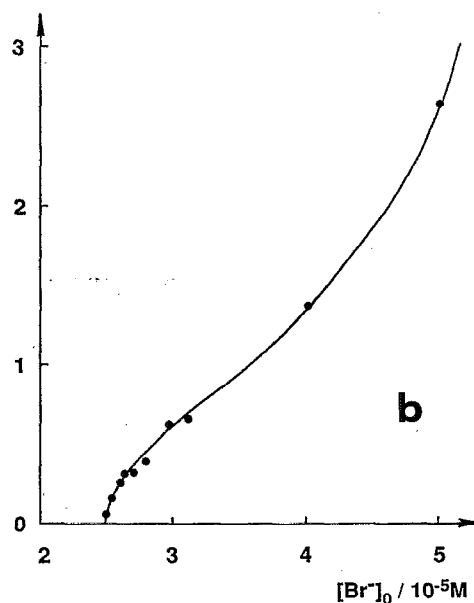


FIG. 4. Perturbation experiments in the excitable state for two levels of $[\text{Br}^-]_0$ in the feedstream, (a) 2.5×10^{-5} M and (b) 5.0×10^{-5} M. No oscillations are observed for $[\text{Br}^-]_0 > 2.5 \times 10^{-5}$ M, but the system is excitable, as can be seen from the response to injections of NaBrO_2 —a perturbation above a sharp threshold results in a single oscillation (the time of injection of a perturbation is indicated by an arrow). At the higher bromide concentration the threshold of excitability is higher; compare (a) and (b).

FIG. 5. (a) The "shoulder" duration (the time the system spends between bromide electrode potentials 187 and 197 mV) and (b) the threshold of excitability (the smallest initial sodium bromite concentration $[\text{NaBrO}_2]_0$ in the reactor that is able to produce a single oscillation in the excitable state), as a function of $[\text{Br}^-]_0$. The shoulder duration increases sharply and the threshold of excitability drops to very small values in the neighborhood of the bifurcation point, as in a saddle-node infinite period bifurcation. The data for the duration of the shoulder are not precise enough to determine the asymptotic law for the divergence, but they are consistent with an exponent of 1/2.

III. RESULTS

A. Experiments with bromide as the control parameter

Bromide was added as a control parameter to feed-stream C. (This was done initially in CFUR experiments to suppress oscillations which interfered with the observability of spiral patterns in the gel, although the spirals actually did not appear to be significantly different for time-independent and oscillatory states in the reservoir.¹⁶) When the bromide flow rate was increased, a characteristic "shoulder" appeared on the oscillatory wave form, as Fig. 3 illustrates.

That width of the shoulder, and consequently the oscillation period, grows rapidly as the point at which the system goes to a steady state is approached; see Fig. 5(a). This behavior is characteristic of a saddle-node infinite period (SNIPER) bifurcation^{3,8,21} and supports the interrupted separatrix model. The nullcline model predicts a Hopf bifurcation without any significant change in period near the bifurcation point.

For input bromide concentrations above a critical value, $[\text{Br}^-]_0 = 2.5 \times 10^{-5} \text{ M}$, no oscillations were observed; the system has a stable steady state and is excitable, as illustrated

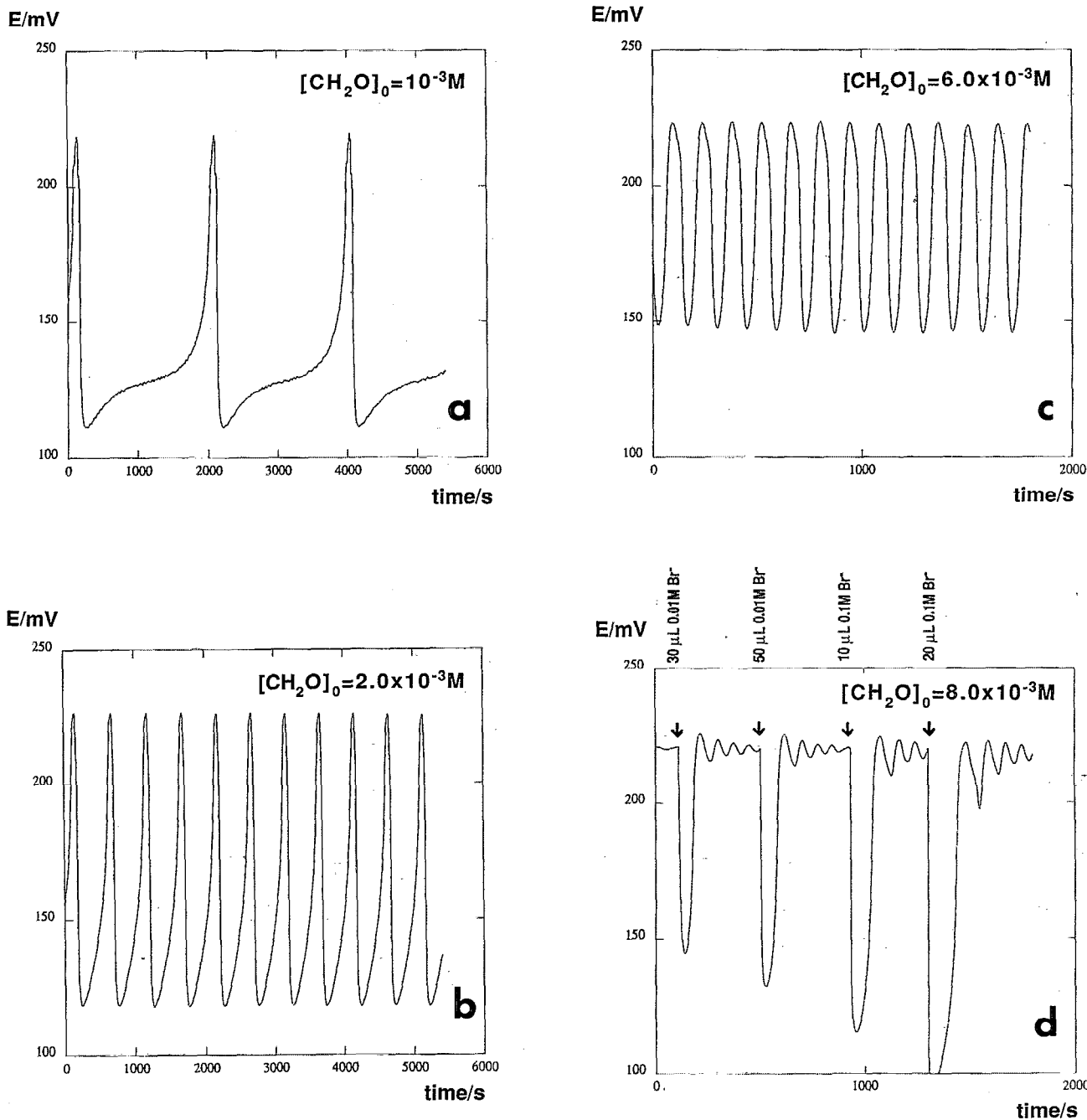


FIG. 6. Experiments with formaldehyde input concentration as a control parameter. (a)–(c) Oscillations with increasing frequency. (d) The oscillations have disappeared and a stable focus has appeared; if this state is perturbed by injecting bromide ions, the response is always a damped oscillation. No excitability was observed. These observations suggest a Hopf bifurcation.

by the experiments shown in Fig. 4. When the amount of NaBrO_2 solution injected into the system is below a well-defined threshold, the system relaxes back to its stable steady state within few minutes. However, for perturbations above that threshold, the response of the system is quite different—it follows a path that resembles a single oscillation, and the

return to the stable steady state requires more than half an hour.

The threshold for excitability decreases continuously to zero as the bifurcation point is approached from the high side; see Fig. 5 (a). This is exactly what happens in the case of a saddle-node infinite period bifurcation, and thus the

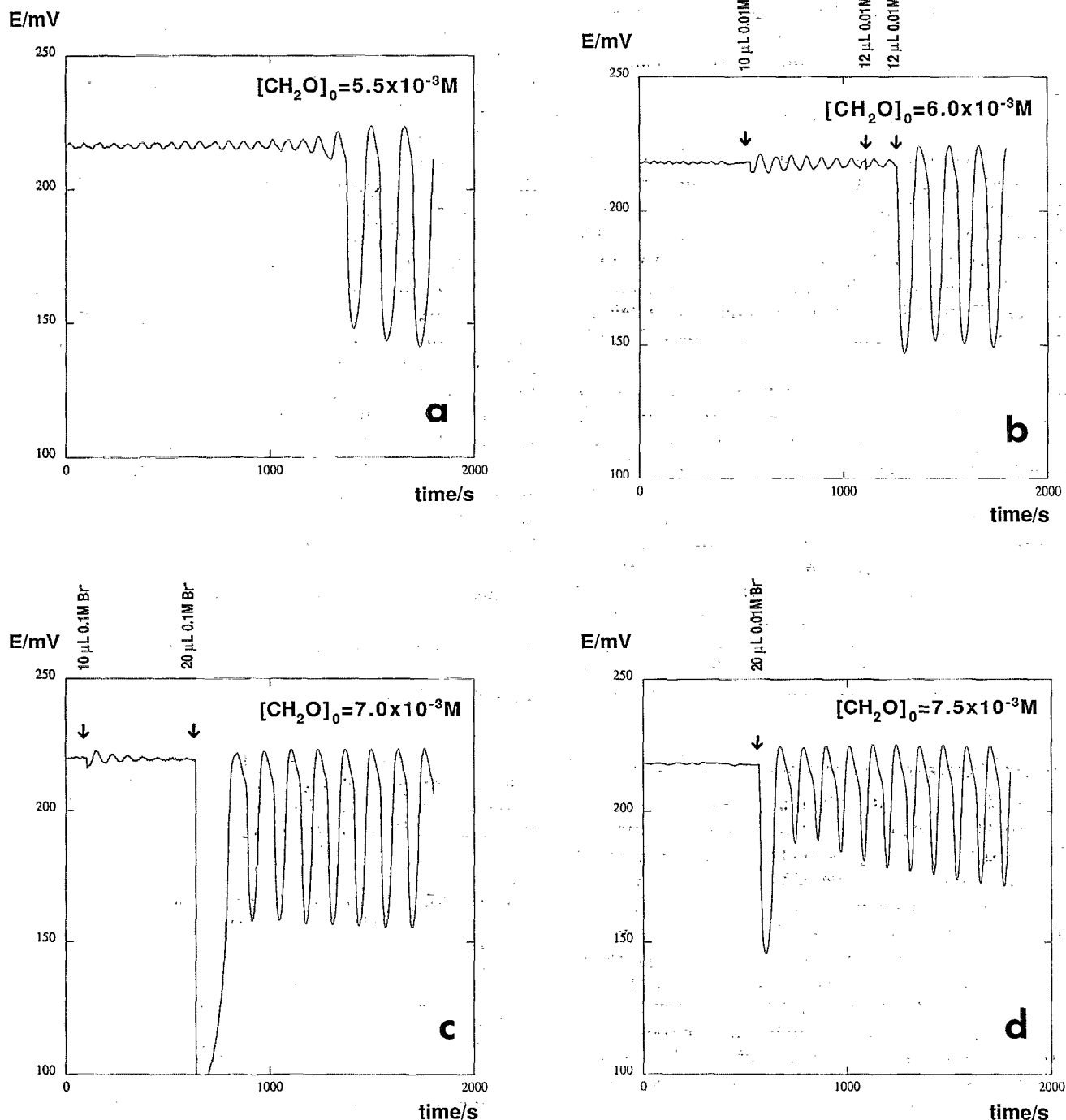
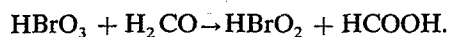


FIG. 7. Bistability between a stable steady state and limit cycle oscillations in the parameter range of $6.0 \times 10^{-3} \text{ M} < [\text{CH}_2\text{O}]_0 < 7.5 \times 10^{-3} \text{ M}$. (a) The initially stable steady state gradually loses stability and oscillations appear spontaneously when the control parameter is decreased gradually from $[\text{CH}_2\text{O}]_0 = 8 \times 10^{-3} \text{ M}$ to $5.5 \times 10^{-3} \text{ M}$; the system is monostable. (b)–(d) Bistability. Perturbations below a threshold decay to the steady state, while perturbations above the threshold produce stable oscillations.

interrupted separatrix model again gives a good description of the experimental situation.

B. Experiments with formaldehyde as the control parameter

The interrupted separatrix picture requires the existence of a saddle and an unstable focus or node in addition to the stable fixed point. The experiments described in the previous section demonstrated the existence of the saddle point. In experiments using formaldehyde concentration as a control parameter, we have also found evidence of an unstable focus. As was demonstrated in Ref. 20, formaldehyde reacts with acidic bromate bromate, producing bromous and formic acids:



While formic acid is an inert product of the BZ reaction, bromous acid is not; it is the autocatalytic intermediate. Thus adding formaldehyde to the system introduces an additional source for the autocatalytic intermediate, while adding bromide to the system has the opposite effect. Bromide is a sink for bromous acid since bromide reacts with bromous acid in a fast reaction. It has been shown that formaldehyde and bromide have opposite effects on the dynamics of the BZ reaction.²⁰

Increasing formaldehyde concentration from zero, a subcritical Hopf bifurcation is found. Above that critical value of the parameter the stable limit cycle disappears and a transition is made to a steady state which is a stable focus; see Fig. 6. The stable limit cycle and a stable focus coexist over a certain parameter range, indicating that the bifurcation is subcritical. This bistability can be revealed either by the hysteresis or by perturbation experiments, as shown in Fig. 7. The stable stationary state produced by the subcritical Hopf bifurcation is *not* excitable. Increasing perturbations of the system always produce qualitatively the same response—damped oscillations toward the stable steady state; see Fig. 6(d). This behavior also shows that this stable steady state is a focus.

C. Choosing between the two models of excitability

The experiments with different control parameters (bromide and formaldehyde) and with different perturbants (NaBrO₂ and bromide) suggest that the excitable behavior of the system studied here is described better by the interrupted separatrix model than by the simple nullcline model. This result, of course, does not imply that the interrupted separatrix model always gives a more realistic description of excitable chemical systems. Any particular dynamical system should be studied experimentally before deciding which model is the better fit. Our work demonstrates the possibility of choosing between theoretical models of excitability based on the comparison of the models of excitability and the experimental observations.

IV. DISCUSSION

In this work we have presented two different pictures of excitability: one with a sharp threshold, and another with a

narrow but finite threshold region. The models discussed here were relatively simple. More complex multidimensional models can also be constructed.²²⁻²⁴ Furthermore, it is not necessary to restrict the definition of excitability to asymptotically stable steady states. As Winfree² says, "Note that excitability is not incompatible with spontaneous oscillation." For example, if we consider limit cycle oscillations of the type depicted in Fig. 3(d), such a system would be very sensitive to perturbations when the "shoulder" region is approached. In this case subcritical perturbations that advance the system closer to the shoulder would not eliminate the long "shoulder" regime. Somewhat larger but supercritical perturbations would, on the other hand, produce a large phase advance because these perturbations help the system jump over the long shoulder regime. Thus various kinds of excitability might exist. All of them, however, should fall into two distinct categories: one with a sharp threshold and the other with a relatively narrow but continuous threshold region. It is difficult to define excitability precisely, but in the case where there is a sharp threshold we offer the following definition: *A dynamical system is excitable if it has a fixed point or periodic attractor having a basin of attraction within which interrupted separatrices or separatrix surfaces can be found.* In practice, the distinction between interrupted separatrix excitability and excitability with a narrow threshold region may often be difficult to establish, and in many situations the simple nullcline picture will continue to provide a very useful description of both situations.

An excitable system might have more than one attractor and consequently other separatrix surfaces as well. The important feature is that at least one separatrix surface can be found *within* a basin of attraction, and that separatrix surface should be somehow interrupted. For the sake of simplicity only point and periodic attractors have been considered in our definition since for chemical systems point and periodic attractors are by far the most common.

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