Universality, multiplicity, and the effect of iron impurities in the Belousov-Zhabotinskii reaction


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In experiments on the Belousov-Zhabotinskii reaction in a flow reactor we have observed dynamical behavior that is described well by one-dimensional maps with a single maximum. A sequence of period doubling bifurcations was observed as a parameter was varied, and beyond the accumulation point for the period doubling sequence there was a sequence of periodic states that has the same symbolic dynamics as the states of the U (universal) sequence of Metropolis, Stein, and Stein (1973). However, in another experiment with malonic acid from a different vendor, we found that some states with particular symbol sequences occurred in three different parameter ranges rather than in one range as in the U sequence. Analysis of the effect of impurities in the reagents showed that some impurities (e.g., Fe$^{3+}$ and esters of malonic acid) at concentrations of only a few ppm produced dramatic changes in the dynamics; such impurities are contained in commercially available malonic acid. Experiments with purified malonic acid indicate that the Fe$^{2+}$/Fe$^{3+}$ and Cu$^{2+}$/Cu$^{+}$ redox couples act as co-catalysts of the Belousov-Zhabotinskii reaction; their effect can be explained by a free radical mechanism. Other metal ions (e.g., Ni$^{2+}$ and Co$^{2+}$) at low concentrations have negligible effect on the dynamics. Finally, both the sequences with universal ordering and the sequences with multiplicity are described well by indented trapezoid maps of the type analyzed by Beyer, Mauldin, and Stein (1986).

I. INTRODUCTION

Recent experiments on the Belousov-Zhabotinskii (BZ) reaction in stirred flow reactors have revealed a broad variety of dynamical phenomena, including a period doubling sequence: when the flow rate of the chemicals through the reactor is varied, a critical value is reached at which the period of oscillation doubles, and a further change in flow rate leads to a sequence of such period doubling transitions. The simplest mathematical systems with period doubling sequences are unimodal (single extremum) one-dimensional (1D) maps. Feigenbaum and others have shown the period doubling sequence for 1D maps with a quadratic extremum has universal properties, that is, the behavior is determined by the nature of the map extremum and not by the global structure of the map. The theory predicts that the bifurcation parameter range between successive period doublings should decrease by a universal factor, 4.669..., as the accumulation point for the sequence is approached. It has been conjectured that period doubling sequences for dissipative dynamical systems in general, even those with many degrees of freedom, should exhibit the same qualitative properties as the period doubling sequence of 1D maps. Experimental observations on diverse physical systems support this conjecture, but detailed comparison with theory is quite difficult because the period doubling sequence converges so fast that in practice it is not possible to observe more than a few period doubling transitions.

This paper concerns the rich dynamical behavior that is found beyond the accumulation point for the period doubling sequence. This accumulation point marks the onset of chaos, but within the chaotic region following the period doubling sequence there are many bifurcation parameter ranges in which the behavior is periodic. Myrberg (1963) and Metropolis, Stein, and Stein (1973) examined these periodic states for several unimodal 1D maps on the interval [0,1] of the form

\[ X_{n+1} = f(X_n) = \lambda g(X_n) \quad \text{,} \]

where \( \lambda \) is the bifurcation parameter. Metropolis, Stein, and Stein (MSS) described a procedure for determining the properties and the ordering of the periodic states. Each map they considered yielded the same sequence; hence they called it the universal sequence or U sequence. We will discuss some properties of the U sequence in Sec. II. The logistic map,

\[ X_{n+1} = aX_n (1 - X_n) \quad \text{,} \]

and many other maps exhibit the U sequence, but necessary conditions for a map to exhibit this sequence are not known and are currently a subject of active research in mathematics. The universality of the U sequence is a qualitative universality—it concerns not the size of the parameter ranges for the different periodic states or the spacing between the states, but the ordering of these states over a large range in bifurcation parameter. In contrast, the universality of the period doubling sequence is quantitative, but it applies only...
asymptotically—in the limit as the period doubling accumulation point is approached.

There is no a priori reason to expect that the BZ reaction with its more than 30 chemical species should exhibit dynamical behavior described by a 1D map. However, several experiments have found conditions in which the behavior is described well by 1D maps constructed from time series for the reaction. Moreover, a 1982 experiment revealed, beyond the period doubling accumulation point, a sequence of periodic states with properties and ordering in remarkably good accord with the universal sequence of Metropolis et al.

The original goal of the present study was to examine in detail the U sequence in the BZ reaction. To this end the apparatus used in our previous studies was refined in several ways to achieve greatly improved control of the experimental conditions. To our great surprise, we then observed a different type of sequence when measurements were made for ostensibly the same experimental conditions that had previously yielded the U sequence. As shall be described, the difference has been found to arise from impurities at the ppm level in the malonic acid samples. The mechanism of the BZ reaction has been studied more extensively than that of any other oscillating chemical reaction, but to our knowledge the extreme sensitivity of the dynamics to trace contaminants of malonic acid that we have discovered has not been previously observed.

We have found that the different sequences of periodic states observed beyond the period doubling accumulation point can all be described by 1D maps. Before presenting our results in detail, we begin by showing in Fig. 1 examples of two distinctly different types of 1D maps that we have observed. (These maps were constructed from time series data by the method to be described in Sec. III B.) In both cases the data are described well by smooth single-valued curves, that is, one-dimensional maps. This is not the case for the BZ reaction in general—for many experimental conditions (different from those considered in this paper) the dynamical behavior is not simply related to 1D maps. The maps in Fig. 1 correspond to chaotic, not periodic, behavior. Although this paper concerns the periodic states, the observations of the chaotic states are important in that they enable us to see the shape of the underlying map. We have discussed elsewhere the correspondence between the observations of chaos and the chaotic behavior of the 1D maps.

The principal goal of this paper is to understand how the different maps in Fig. 1 and the sequences given by these maps arise. We have found that malonic acid reagents from different vendors all yield unimodal maps, but the width of the peak and the depth of the indentation to the right of the peak is different for malonic acid samples from different sources. The U sequence of periodic states is observed for the maps with a shallow indentation (broad peak), but in the experiments that yielded deeply indented maps, a different sequence was observed: some periodic states were observed in three different flow rate ranges rather than in one range as in the U sequence. We will refer to this behavior as multiplicity.

After reviewing some properties of 1D maps and the U sequence in Sec. II and the experimental procedures in Sec. III, we will describe the observations of the U sequence in Sec. IV and a sequence with multiplicity in Sec. V. A model 1D map, an indented trapezoid, that gives insight into both of the observed sequences will be presented in Sec. VI. The effect of chemical impurities will be discussed in Sec. VII, and the conclusions drawn from this work will be given in Sec. VIII.

II. ONE-DIMENSIONAL MAPS AND THE U SEQUENCE

In our discussion of the properties of unimodal 1D maps and the U sequence, we have in mind the logistic equation (2) as an example. Even for the logistic equation much of the evidence for different properties has been obtained from numerical studies—mathematically rigorous results are quite difficult to achieve.

We first consider the mechanics of map iteration, which is illustrated in Fig. 2. For a given value of $\lambda$ one picks any initial condition (except for a set of measure zero) and iterates the map until transient behavior disappears. Further behavior of the sequence $x_n$ can be either periodic or chaotic. We will discuss only the periodic states. For categorizing attracting periodic states it is sufficient to consider the iterates of a point $X_0$, where $f(x)$ is the maximum of the map. [The maximum of the map is actually visited only for a single value of the bifurcation parameter (the "super-stable orbit") in the parameter range in which a particular periodic state is stable, but for categorizing the periodic states it is sufficient to consider this bifurcation parameter value.] Each periodic state can be described by a symbol sequence of $L$'s and $R$'s, where the $n$th symbol specifies the location (to the left or right of $X_0$) of the $n$th iterate of $X_0$. 

![Figure 1](image-url)
Thus, for example, the 4-cycle in Fig. 2 is described by the sequence "RLR", where a symbol for the initial condition $X_0$ (neither $R$ or $L$) is omitted.

Metropolis, Stein, and Stein\textsuperscript{4} used a method called symbolic dynamics to deduce from the single extremum property of the map the symbol sequences for the periodic states and the order in which the states occur as a function of bifurcation parameter $\lambda$. For small $\lambda$ the map has a fixed point (1-cycle). If $\lambda$ is increased, the 1-cycle eventually loses its stability to a 2-cycle, and with further increase in $\lambda$, the 2-cycle loses stability to a 2\textsuperscript{2}-cycle, and so on. This infinite sequence of period doubling transitions converges to a $2^n$-cycle at a finite $\lambda = \lambda_c$.

Fundamental cycles, that is, periodic states not arising from period doubling, occur for all integer periods $k$ beyond the period doubling sequence for the first fundamental, the 1-cycle. Each of these $k$-cycles gains stability at a tangent bifurcation and loses stability through period doubling. As an example of the period doubling, consider the fundamental 4-cycle (RLL), which is distinct from the 4-cycle RLR that arises from successive doublings of the 1-cycle. At the end of the interval in $\lambda$ in which the fundamental 4-cycle is stable, it successively doubles to give $4 \times 2^n$-cycles for all positive $n$. The convergence rate for each such period doubling sequence is the same as for the original sequence; that is, for large enough $n$ the bifurcation parameter range for the state with period $k \times 2^n + 1$ is 4.669... times smaller than the bifurcation parameter range for the state with period $k \times 2^n$. Each allowed state, defined by a particular symbol sequence, occurs for only one interval in $\lambda$, and at any given bifurcation parameter value not more than one periodic state is stable.\textsuperscript{19}

The number of states allowed by the symbolic dynamics theory increases very rapidly with increasing $k$. For example, there are three distinct 5-cycles ($RLRR$, $RLLR$, and $RLLL$), and 1091 distinct 15-cycles.\textsuperscript{20} All possible orders of visitation occur and are stable for some parameter interval.\textsuperscript{21} Hence the range in $\lambda$ over which a state is stable decreases extremely rapidly with increasing $k$, so that in practice it is not possible to observe states with large $k$. Recognizing this, Metropolis, Stein, and Stein listed in the order of occurrence all 209 $U$ sequence states with $k < 11$, where the choice of $k = 11$ for the cutoff, rather than a larger or smaller value of $k$, was entirely arbitrary. Despite the arbitrariness of the numbers denoting the position on the list of states with $k < 11$, these so-called MSS numbers provide a convenient way to refer to the ordering of the $U$ sequence states, and we will use them in describing our results. Of course, between any two fundamental states with successive MSS numbers, there is an infinite number of $U$ sequence states with $k > 11$. In fact, the set of all bifurcation parameter values corresponding to stable periodic states is believed to be dense. However, at the same time the parameter values corresponding to chaotic states have positive measure.\textsuperscript{22} Numerical evidence indicates that for the logistic map 89% of the $\lambda$ values between the accumulation point for the period doubling sequence [$a = 3.57...$ in Eq. (2)] and the end of the $U$ sequence [$a = 4$] correspond to chaotic states.\textsuperscript{23}

Table I lists all $U$ sequence states with $k < 6$. To illustrate the rapid decrease in parameter range in which states with increasing $k$ are stable, we show for two particular maps the (map-dependent) range in bifurcation parameter for each state.

Recently Beyer, Mauldin, and Stein\textsuperscript{24} have examined the problem of finding the necessary conditions for a map to yield the $U$ sequence. They discovered a surprisingly simple map that yielded a sequence different from the $U$ sequence. We will return to this question in Sec. VI.

III. EXPERIMENTAL PROCEDURES

A. Instrumentation

Our measurements were made in a continuously stirred tank flow reactor. The bifurcation parameter was the residence time $\tau$, which is the average time the chemicals spend in the reactor ($\tau = V / f$, where $V$ is the reactor volume and $f$ is the total flow rate of the three feeds). The concentrations of the chemical feeds were held fixed. The flow rate was initially controlled with peristaltic pumps and later with dual piston pumps. We should emphasize immediately that the observation of different types of dynamical behavior had nothing to do with the pumps: for the same chemistry the same behavior was found with both peristaltic and piston pumps, the only difference being that the stability of the flow rate was more than an order of magnitude better for the piston pumps than it was for the peristaltic pumps.

The concentrations of the feed chemicals in our reactor were as follows: malonic acid, 0.25 M; potassium bromate, 0.10 M; cerous sulfate, 0.000 83 M; and sulfuric acid, 0.20 M. The malonic acid, potassium bromate, and cerous sulfate were fed separately with equal concentrations of sulfuric acid in each of these feeds. The flow rates for the three feeds were carefully adjusted to be equal and were then varied in concert.

The bromate as received contained 0.04% to 0.10% by weight bromide, a concentration large enough to affect the dynamics dramatically. Therefore, to ensure a minimal bro-
mide concentration in the feed, we always used potassium bromate that was recrystallized twice from water.

Malonic acid samples (> 99.5% purity) from different vendors were found to yield qualitatively different dynamics. This is one of our major results, and it will be discussed in Sec. VII.

In flow reactors the most difficult parameter to control precisely is the flow rate. Long term stability was crucial in our experiment for two reasons: (1) The residence time of about 1 h required a wait of several hours to be sure that transients had decayed after a change in flow rate. (2) To distinguish high period periodic states from chaotic states it was necessary in some cases to observe a state for several hundred oscillations, which was many hours for the typical oscillation period of 2 min.

Our initial experiments with peristaltic pumps were clearly limited by the inevitable drift in this type of pump; moreover, worse yet, the drift was different for each channel of the multichannel peristaltic pump. We then switched to dual piston metering pumps (LDC Cheminert CMP-1K) modified with a stepping motor speed control. In these pumps only Teflon, Kel-F, and borosilicate glass (the pistons) come into contact with the pumped fluids. Extensive tests showed that these piston pumps have excellent long term stability: measurements by weighing showed that the standard deviation in the flow rate was less than 0.2% for times ranging from 10 min to 24 h. Another advantage of these piston pumps is that they produce only a very small pulsation in flow rate corresponding to the periodic switching between the two pistons; in contrast, the peristaltic pumps produce noticeable periodic pulsations (evident, for example, as a component in the bromide ion potential power spectra). However, runs with different tube sizes (which give different pulsation frequencies) in the peristaltic pump and with the piston pump for the same chemistry made it clear that even for the peristaltic pumps the dynamical behavor we report in this paper was not a consequence of periodic forcing of the system.

The constancy of the period of oscillation provided another indication of the stability of our system. For a periodic state with one oscillation per period (a 1-cycle) we found that the period of oscillation fluctuated by more than 1% when peristaltic pumps were used, but with the piston pumps the standard deviation in the oscillation period was in most tests only 0.1%, which was comparable to the precision with which we could determine the period from the data.

The solutions passed through 5 μm Teflon filters before entering the pumps, and traps for bubbles followed the pumps. The chemicals then passed through 1 m long Teflon tubes immersed in a temperature-controlled bath (28.01 ± 0.02 °C) and into the reactor, which was then immersed in the bath.

A diagram of the reactor is shown in Fig. 3. The reactor body and all tubes and fittings were made of Teflon or Plexiglas. The overflow lip near the top of the reactor served to maintain a constant reaction volume and to decouple the effluent from the mixture in the reactor; the overflow was removed with an aspirator. The reaction was stirred at 1800 rpm by a synchronous motor.

The bromide ion potential (proportional to the negative of the log of the concentration) was monitored with a specific ion electrode and a double junction gel reference electrode and recorded in a computer. Measurements of the bromide ion potential integrated over successive time intervals of 0.88 s (which gives about 125 data points per oscillation) were made with 14 bit resolution; files of any length could be recorded, but most files had 32 768 points (an 8 h duration).

B. Construction of maps from the data

Figure 4 illustrates how we obtain 1D maps from the time series data for the bromide ion potential. The maps were constructed simply by determining the magnitudes
of the successive minima in the time series, \( X_1, X_2, \ldots, X_n, X_{n+1}, \ldots \), and then plotting each minimum as a function of the previous minimum, thus obtaining \( X_{n+1} \) vs \( X_n \). Alternatively, we could have constructed phase portraits and obtained maps from a sequence \( \{X_n\} \) obtained from a Poincaré section, as in Refs. 15 and 16. However, the next amplitude maps were simpler to construct, contained the same information, and had as good a signal-to-noise ratio as the maps constructed from the Poincaré sections.

A periodic state was used in Fig. 4 to illustrate the construction of maps, since for a low period periodic state the full iteration process can be shown. However, the shape of the 1D map can be seen more clearly in data for a chaotic state, as Fig. 1 illustrates.

IV. OBSERVATIONS OF THE U SEQUENCE

The first unimodal 1D map we observed was the broad peaked map shown in Fig. 1. It was then realized by Roux et al.\(^1\) that it should be possible to observe a period doubling sequence. At somewhat smaller values of \( \tau \) than those that yielded the maps in Fig. 1, a stable oscillatory state with one oscillation per period was found, as shown in Fig. 5(a). The value of \( \tau \) was then increased in small steps until a critical value was reached at which the period doubled; the amplitude of successive oscillations alternated between two values, as shown in Fig. 5(b). With further increase in \( \tau \), another period doubling transition was reached, resulting in the period 4 state shown in Fig. 5(c). With a very slight increase in \( \tau \), a period 8 state was observed. A few cycles of period 16 were observed in some runs, but the system was not sufficiently stable to observe the period 16 state for long

FIG. 3. The reactor, which, except for the probes and inlets, is cylindrically symmetric. The reactor volume is 33.0 cm\(^3\).

FIG. 4. (a) Time series for the bromide ion potential measured for a period 5 state (after all transients have decayed). (b) The data points obtained by plotting successive minima in the time series are superimposed on the underlying map obtained from a nearby chaotic state. (Successive maxima yield a similar map, but that map has a poorer signal-to-noise ratio.) The figure shows that the symbolic representation for this state is RLR\(^2\).

FIG. 5. Bromide ion electrode potential time series illustrating the period doubling sequence: (a) \( \tau = 0.725 \text{ h} \), period 1; (b) \( \tau = 0.773 \text{ h} \), period 2; and (c) \( \tau = 0.803 \text{ h} \), period 4. The dots above the time series are separated by one period.
periods of time. This is not surprising since the range of \( \tau \) in which the period 2 state was stable was less than 2\%, and according to the theory of period doubling for 1D maps, the range of stability of each successive periodic state decreases by 4.669\ldots (in the asymptotic limit of a large number of transitions); hence the stability range for the period 16 state would be less than 0.02\%.

Many periodic states were observed when \( \tau \) was increased beyond the region of the period doubling sequence.\textsuperscript{16} Time series records for some of the states are shown in Fig. 6, and the states with \( k < 6 \) are listed in Table I. The data in Fig. 6 were obtained with a peristaltic pump, so there was an inevitable slow drift in \( \tau \); our records contain short segments of many longer period U sequence states. In all cases the periodic states observed in the same file were found to be close together in the U sequence.

Although the bifurcation parameter interval over which a particular state is stable is map dependent, in general it decreases very rapidly with increasing period, as mentioned previously and as illustrated for two maps in Table I. The exponential map in Table I is rather similar to the experimental map with the broad peak shown in Fig. 1. In fact, we observed every U sequence state of the exponential map that has an interval greater than 1.4\% of the interval for the period 3 state, except for the RL \textsuperscript{4} state (MSS number 178), which occurs after the termination of our observed sequence; no states of the exponential map with intervals less than 1.4\% of the interval for the period 3 state were observed. We observed no U sequence states with MSS numbers greater than 147.

In summary, the observed periodic states were all found to be allowed states of the U sequence, and the order in which they occurred as a function of \( \tau \) was completely consistent within the experimental resolution with that given by Metropolis et al. for U sequence states.

V. MULTIPLICITY

The remarkable agreement found between the sequence of periodic states observed for the BZ reaction and the U sequence, described in the previous section, left us quite unprepared for the results of the next experiment. The control of the experiment was improved in several ways, and then the previous experiments were repeated with ostensibly the same conditions (but with chemicals from a different vendor). Again a sequence of periodic states was observed, and again each of the observed states was one of the allowed states of the U sequence.\textsuperscript{17} However, in this new experiment some of the states occurred in three different intervals of \( \tau \)—this multiplicity is illustrated in Fig. 7, and the order of occurrence of all the states observed in this sequence is shown in Fig. 8.

States with the same symbol sequence that were observed in three different parameter intervals had underlying maps which were the same in shape but varied in height. The height of the maps was found to increase monotonically with \( \tau \), as shown in Fig. 9.

In the U sequence each state gains stability at a tangent bifurcation and loses stability through period doubling (a pitchfork bifurcation). In contrast, in the sequence with multiplicity a state at its second occurrence gains stability through reverse period doubling and loses stability at a tangent bifurcation. This reverse period doubling into a stable state can be seen for the RL state in Figs. 7(e) and 7(f); this contrasts with the forward period doubling out of the first RL state, which can be seen in Figs. 7(a) and 7(b).

We were obviously concerned when experiments for ostensibly the same conditions yielded qualitatively different dynamics. A detailed analysis of the chemicals showed that the difference in the dynamics arose primarily from impurities in the malonic acid, as we will discuss in Sec. VII, but first we will show how the different observed dynamical behaviors can be modeled by a simple 1D map.

VI. MODEL MAPS

A. The Indented trapezoid

Recently Beyer, Mauldin, and Stein\textsuperscript{24} reported the first study of multiplicity of the periodic states of 1D maps. Although the U sequence had only been proved to occur for
FIG. 7. Several periodic states observed in the experiments with multiplicity discussed in Sec. V are shown in the order in which they occurred as a function of increasing \( \tau \). The periods and the MSS numbers for each state are shown above the time series. One-dimensional maps from these data have a deep indentation; see the narrow peaked map in Fig. 1. The dots above the time series are separated by one period.

FIG. 8. The order of the periodic states in the observed sequence with multiplicity is shown as a function of the control parameter \( \tau \). The data points shown are in the middle of the interval in \( \tau \) in which a periodic state was observed. The smooth solid curve connecting the data points is drawn to guide the eye. The U sequence would (by definition) be given by a monotone increasing curve. In contrast, states here with MSS numbers greater than about 29 occur for three different intervals of \( \tau \).

parabolic and trapezoidal maps and conjectured for concave maps, they nevertheless found it surprising that a map as simple as a piecewise linear “indented trapezoid” exhibited multiplicity. Motivated by their paper, we have examined the dynamics of indented trapezoid maps that approximate the maps obtained in our experiments. The map we have studied is shown in Fig. 10. It is similar to the indented trapezoid of Beyer et al. (see their Fig. 9.2) except that our maps, being constructed to fit the observed maps as closely as possible, are not symmetric about \( X = 0.5 \).

The experimental maps throughout the range of the periodic sequence are reasonably well approximated by Eq. (1), where \( g(X) \) is an indented trapezoid. Three sets of data are compared in Fig. 11 to an indented trapezoid. All of the data are found to be fairly well described by Eq. (1) with the same \( g(X) \); the parameter values defining this \( g(X) \) are given in Fig. 10.25

The symbolic dynamics of the observed sequence with multiplicity is in complete accord with the dynamics of the indented trapezoid in Fig. 10. That is, the observed states occur in precisely the same order as the states of this indented trapezoid. The comparison can be seen in Fig. 12.

Insight into the transition in the behavior of the map from one which yields the U sequence to a map which yields a sequence with multiplicity can be understood by examining the dynamics of the indented trapezoid of Fig. 10 as a function of the height of the indentation \( h \) with the other map parameters held fixed. For \( h = 0.893 \) there is no indentation, the map is simply a trapezoid, and the U sequence is obtained, as found by Metropolis et al. When \( h \) is reduced,
indenting the trapezoid, the U sequence persists for \(0.62 < h < 0.893\). However, a further decrease in \(h\) leads to multiplicity, as Fig. 13 illustrates. Then some states occur for three parameter intervals in \(\lambda\). For \(h = 0.09\) the map yields a sequence in accord with the observed sequence described in Sec. V. Moreover, the aforementioned behavior of the second occurrence of a periodic state can be understood from Fig. 13: a state gains stability for the second time (with increasing \(\lambda\)) through reverse period doubling, and loses stability at a tangent bifurcation; this is just the behavior indicated by the experiments.

**B. Cubic spline fit map**

We have also fit the maps obtained in the experiments to cubic splines and then studied the periodic sequences for those maps. Our curve fitting programs used the IMSL routine ICSFKU (which is a least squares approximation by cubic splines with fixed knots); we obtained our best fits with five unequally spaced knots. Once again, the same function \(g(X)\) was found to fit the periodic and chaotic data throughout the entire parameter range studied. The spline-fit \(g(X)\) yields exactly the same symbolic dynamics as the indented trapezoid map of Fig. 10; see the dashed curve in Fig. 12. However, as might be expected, although the two maps yield the same states in the same order, the actual magnitudes of the separations between the observed periodic states are de-

**FIG. 11.** One-dimensional maps constructed from the laboratory data for (a) \(\tau = 0.757\ h\), (b) \(\tau = 0.769\ h\), and (c) \(\tau = 0.817\ h\) are compared with the indented trapezoid map of Fig. 10 (with \(\lambda = 0.220, 0.472, \) and 0.713 for (a)--(c), respectively).
Extensive analyses of the malonic acid samples show that, although there are many impurities at the ppm level, the differences in the dynamical behavior appear to arise primarily from iron and from esters of malonic acid. (The iron probably comes from the activated charcoal used in producing and purifying the malonic acid.) The behavior is rather insensitive to the other impurities that are present (detected impurities include, for example, fairly large amounts of Ba$^{2+}$ in some samples and Ca$^{2+}$ in others; no halogen impurities were detected).

Malonic acid was purified by two independent procedures, each using three recrystallization steps. The purified malonic acid samples were all found to yield the same dynamical behavior, independent of the source of malonic acid and independent of the purification procedure. A detailed description of the purification procedures and the effect of impurities on the dynamics will be reported elsewhere, but to illustrate the importance of impurities and the subtle nature of the effects we will present some results showing the effect of added iron.

The addition of small amounts of Fe$^{3+}$ to the feed stream shifts and modifies the transition sequence, as Fig. 14 illustrates. A concentration of less than $10^{-5}$ M in the reactor, which is more than two orders of magnitude smaller than the cerium catalyst concentration, produces a substantial change in the dynamics! The effect of iron on the dynamics of the BZ reaction in a batch reactor was previously observed by Nagashima.

The effect of added iron on the 1D maps is illustrated in Fig. 15: purified malonic acid yields a map with a deep indentation, as shown in Fig. 15(a), while the addition of iron results in a shallower indentation, as shown in Fig. 15(b). Figures 15(a) and 15(b) were obtained for different $r$; Fig. 15(c) shows a map corresponding to the same $r$ as Fig. 15(b).

Some commercially available malonic acid reagents yield maps with a deep enough indentation to result in multiplicity; the narrow peaked map in Fig. 1 is an example. However, we have found no commercially available malonic acid that gives a map with an indentation as deep as the one in Fig. 15(a).

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**VII. EFFECT OF IMPURITIES**

**A. Identification of the impurities**

Chemical analyses of the different reagents and of the water used in mixing the solutions indicate that the observed differences in dynamical behavior arose from very small amounts of impurities in the malonic acid samples supplied by different vendors. Malonic acid samples (99.5% purity) from seven different vendors were each found to yield different dynamics and different 1D maps. Even different lot numbers from the same vendor yielded different behavior! Nevertheless, the results with any given sample were reproducible over long periods of time and reproduced in experiments with a different apparatus.

FIG. 15. (a) A map obtained with purified malonic acid in the BZ reaction. No commercially available malonic acid samples have been found that yield such a deeply indented map, but all the malonic acid reagents we have examined yield this map after being carefully purified. (b) A map with a shallower indentation, obtained after adding only 24 ppm (weight fraction) of Fe$^{3+}$ to purified malonic acid in the BZ reaction. Maps (a) and (b) were obtained at similar points within the transition sequence, which means the maps correspond to different $r$ because of the shift in the sequence (see Fig. 14); for comparison, a map obtained for the same $r$ as in (b) is shown in (c). The conditions for these three maps are shown by the points labeled (a), (b), and (c) in Fig. 14.
**B. Iron as a co-catalyst**

The large effect found for small amounts of added iron is surprising since the uncomplexed iron alone is not a catalyst of the BZ reaction.\(^{29}\) We conjecture that the Fe\(^{2+}\)/Fe\(^{3+}\) redox couple acts as a kind of co-catalyst in the BZ reaction by changing the free radical pathways in the reaction. It is easy to imagine that the ferrous ions will be oxidized in the strong oxidizing medium of the BZ reaction, but it is less clear how reducing agents can appear in the same medium to reduce the resulting ferric ions. However, free radicals are present, and they can reduce Fe\(^{3+}\) fairly easily\(^{29}\) by the following mechanism:

\[
\text{Fe}^{3+} + \text{R} \cdot + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{ROH} + \text{H}^+ ,
\]

where R \cdot would be some organic free radical, e.g., malonyl radical (MA \cdot).\(^{30}\) The reduction reaction would be followed by a reoxidation of Fe\(^{2+}\) by acidic bromate or by Ce\(^{4+}\). Ganapathisubramanian and Noyes\(^{31}\) and Brusa et al.\(^{30}\) have pointed out that malonyl radicals are not oxidized by Ce\(^{4+}\); therefore, iron could catalyze that reaction:

\[
\text{Fe}^{3+} + \text{MA} \cdot + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{TTA} + \text{H}^+ ,
\]

\[
\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{3+} ,
\]

where TTA is tartronic acid. Thus the net reaction would be

\[
\text{Ce}^{4+} + \text{MA} \cdot + \text{H}_2\text{O} \rightarrow \text{Ce}^{3+} + \text{TTA} + \text{H}^+ .
\]

An approximate way to take reaction (4) into account would be through the stoichiometric factor \(f\) in the fifth step of the Oregonator model of Field and Noyes\(^{32}\) [2Ce\(^{4+}\) \rightarrow fBr\(^{-}\)]. Reaction (4) can decrease the factor \(f\) because it consumes Ce\(^{4+}\) without producing bromide ions. A decrease in \(f\) can result in a dramatic change in the reaction dynamics since, as is well known, \(f\) plays an important role in the dynamics.\(^{33}\) The stoichiometric factor could have a special importance for the complex oscillations studied here, since, as was pointed out by Janz et al.\(^{34}\) and investigated further by Rinzell and Troy,\(^{35}\) composite double oscillations and bursting phenomena can be explained by slow variations in \(f\).

There is another way in which reaction (3) can modify the reaction mechanism: the free radicals can act as a control intermediate in the same way as the bromide ion (see Ganapathisubramanian and Noyes\(^{36}\) and Brusa et al.\(^{30}\)). To explore the role of free radicals we have investigated the effect of Cu\(^{2+}\), Ni\(^{2+}\), and Co\(^{2+}\) on the BZ reaction. It is known that Cu\(^{2+}\) easily oxidizes some organic free radicals, while Ni\(^{2+}\) and Co\(^{2+}\) do not,\(^{39}\) but all of these ions (and Fe\(^{3+}\) as well) form different complexes with a wide range of organic and inorganic ligands. We find that adding Cu\(^{2+}\) affects the reaction in a way similar to adding Fe\(^{3+}\), except that the reaction is less sensitive to the copper—the copper concentration must be about twice that of iron to achieve the same effect. In contrast, the addition of low concentrations of Ni\(^{2+}\) or Co\(^{2+}\) has no detectable affect on the reaction. Even when the concentration of these ions exceeds that of the catalyst, only a slight effect is observed (comparable to the effect caused by adding \(10^{-6}\) M of Fe\(^{3+}\)).

We conclude that Fe\(^{2+}\)/Fe\(^{3+}\) and Cu\(^{2+}\)/Cu\(^{2+}\) redox couples act as co-catalysts of the BZ reaction and that their effect can probably be explained by reactions involving organic free radicals. Therefore, a systematic study of the effect of these co-catalysts could help elucidate the role of free radicals in the reaction mechanism.

**VIII. CONCLUSIONS**

We have found that iron and certain esters of malonic acid at concentrations of only a few parts per million can produce a qualitative change in the dynamical behavior of the Belousov–Zhabotinski reaction. This extreme sensitivity of the dynamics to impurities, apparently unobserved in past studies of the BZ reaction, suggests that investigations of the dynamics can provide new insights into the mechanism of the reaction.

Our second principal finding is that a simple one-dimensional map, the indented trapezoid, provides an accurate model of the observed dynamical behavior. Thus our work provides another example of a situation in which a purely mathematical study of a one-dimensional map—in this case that of Beyer et al.\(^{34}\) —yields a simple model for a nonequilibrium physical system with many degrees of freedom.

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In our previous experiments (Ref. 17), conducted before the purified malonic acid was available, some differences in the behavior for Fe$^{2+}$ and Fe$^{3+}$ were observed.

A recent numerical simulation of a seven variable Oregonator-type model of the BZ reaction yielded a deeply indented 1D map similar to that shown in Fig. 15(a); however, the concentrations were rather different for the simulation and our experiment. See P. Richetti, J. C. Roux, F. Argoul, and A. Arneodo, J. Chem. Phys. (submitted).


