Chemical reactions with nonlinear kinetic behavior can give rise to a remarkable set of spatiotemporal phenomena. These include periodic and chaotic changes in concentration, traveling waves of chemical reactivity, and stationary spatial (Turing) patterns. Although chemists were initially skeptical of the existence and the relevance of these phenomena, much progress has been made in the past two decades in characterizing, designing, modeling, and understanding them. Several nonlinear dynamical phenomena in chemical systems provide simpler analogues of behaviors found in biological systems.

I. Introduction

If one were to show a freshman chemistry class two beakers of solution and suggest that after the solutions were mixed the color of the resulting solution would oscillate back and forth between yellow and blue, or that a petri dish full of the stuff would begin to develop concentric rings of blue in an initially homogeneous red bulk, one would be met with considerable skepticism, to say the least. Making the same suggestion to a group of elementary school children turns out to evoke a rather different and more rewarding reaction—curiosity to see these fascinating and beautiful phenomena and eagerness to understand how they come about.

The history of nonlinear chemical dynamics, a field in which the objects of study are chemical reactions that display such phenomena as periodic or chaotic temporal oscillation and spatial pattern formation, resembles a progression, or perhaps we should say a retrogression, from the freshman mindset described above to that of the elementary school child. Published observations of chemical oscillations date back at least to the early nineteenth century,\(^1\) and the discovery of periodic precipitation patterns\(^2\) toward the end of the century was followed by the development of a remarkably accurate formula for the velocity of propagation of chemical waves\(^3\) in 1906. By the early 1920s, Lotka\(^4\) had developed a simple model, based on two sequential autocatalytic reactions, that gives sustained oscillations, and Bray\(^5\) had, albeit serendipitously, discovered the first homogeneous chemical oscillator, the iodate-catalyzed decomposition of hydrogen peroxide.

Although ecologists were quick to pick up on Lotka’s theories, his models, as well as Bray’s experimental work, were met with, at best, indifference by the chemical community. In fact, Bray’s experiments were attacked\(^6\) more often than they were embraced in the chemical literature of the next half century. The vast majority of chemists who thought about the question at all felt that chemical oscillation constituted a violation of the Second Law of Thermodynamics, a sort of perpetual motion machine in a beaker.

This notion that nonmonotonic behavior in chemical systems is somehow contrathermodynamic\(^7\) began to break down, at least on the theoretical side, with the work of Onsager and particularly Prigogine and collaborators\(^8\) on nonlinear thermodynamics beginning in the 1940s. Nevertheless, when the next experimental breakthrough occurred, it still met major resistance. In the early 1950s, B. P. Belousov, a Soviet biophysicist, was seeking an inorganic analogue of the biochemical Krebs cycle when he noticed that the color of a mixture consisting of bromate and cerium ions with citric acid in sulfuric acid oscillated back and forth, with a period of a minute or so, between colorless and pale yellow. Belousov carefully characterized the phenomenon and submitted his results, with recipes included, to a number of journals, all of which rejected them on the grounds that such a thing could not occur. He eventually settled, before leaving the field, for publishing a single short abstract in the unrefereed proceedings of a conference on radiation medicine.\(^9\) Belousov’s recipes circulated among Moscow laboratories, and a young graduate student, Anatol Zhabotinsky, began to study and refine the reaction. Zhabotinsky modified the reagents, discovering that malonic acid could replace citric acid and that the redox indicator ferroin gave a more dramatic red—blue color change than the cerous—ceric couple.\(^10\) He characterized much of the chemistry and showed that, in an unstirred system, the reaction spontaneously gave rise to “target patterns” or spirals of oxidized blue ferrin in an initially homogeneous dish of reduced red ferroin-dominated solution (see Figure 1).\(^11\)

Thanks to the path-breaking work of Zhabotinsky and a 1968 conference on biological and biochemical oscillators in Prague\(^12\) that featured talks and demonstrations on chemical oscillators and patterns, knowledge of what had now come to be called the Belousov—Zhabotinsky (BZ) reaction and its exotic behavior began to filter out to the West. Prigogine’s group in Brussels developed a simple model, dubbed the Brusselator,\(^13\) that was more chemically realistic than Lotka’s abstract model and showed a variety of interesting spatial and temporal phenomena, which they called dissipative structures. The general results of nonlinear thermodynamics, that such behavior could occur in nonlinear systems maintained sufficiently far from equilibrium, were now being brought to reality in specific systems.

A crucial step was the development by Field, Körös, and Noyes (FKN) of a detailed chemical mechanism\(^14\) for the BZ reaction. Numerical simulation of the resulting set of about 20 rate equations\(^15\) confirmed that chemical oscillation could be explained by the same set of chemical kinetics principles that apply to “normal” reactions. Field and Noyes\(^16\) soon managed to abstract from the FKN mechanism a three-variable model,

the Oregonator, that contains the essence of the chemistry while allowing for detailed numerical and analytic investigation.

The developments of the past two decades, many of which are discussed in this article, have included the design of more than two dozen new chemical oscillators, mechanistic elucidation of the chemistry of many oscillating reactions, the discovery of chaos in chemical systems, better theoretical understanding and new experimental configurations for studying chemical waves and patterns, and a growing appreciation of the connections between the phenomena of nonlinear chemical dynamics and the behavior of biological systems.

II. Multistability

The simplest, nontrivial behavior displayed by nonlinear chemical systems is bistability, in which two stable steady states coexist over a range of operating conditions. Typically studied in a continuous-flow, stirred tank reactor (CSTR), bistable systems undergo transitions from one state to another when suitably perturbed or when a control parameter is varied beyond a bistability limit. Early examples include the acidic bromate oxidation of cerium(III), which comprises the inorganic subset of the BZ reaction, and the iodate oxidation of arsenite, a variant of the venerable Landolt clock reaction. Many bistable systems are now known, and the detailed reaction mechanisms of a number have been characterized.

The iodate—arsenite reaction is perhaps unique among nonlinear systems that exhibit bistability and chemical waves in that it can be accurately described in terms of a single dynamical variable. For the CSTR system, the one-variable model is

\[
d[I^-]/dt = (k_a + k_b[I^-])\Gamma(I[O_3^-]_0 + [I^-]_0 - [I^-]) + k_0([I^-]_0 - [I^-])
\]

where \([I^-]_0\) and \([O_3^-]_0\) are feedstream concentrations and \(k_0\) is the reciprocal residence time of the reactor (proportional to the flow rate). The steady-state concentration of iodide as a function of the flow rate can be easily determined by solving the cubic equation when \(d[I^-]/dt = 0\). Perturbations that move the system beyond the unstable steady state (the middle solution of the cubic equation) result in transitions from one stable state to the other, while transitions at the bistability limits occur with relaxation dynamics suggestive of first-order phase transitions.

Other patterns of steady-state multiplicity are possible. A simple modification of the CSTR feedstreams in the iodate—arsenite system gives rise to mushrooms and isolas. Specifically, a second, independent flow of solvent (buffer solution) is introduced which causes a dilution of the reactants at long residence times. A mushroom is comprised of two regions of bistability, as shown in Figure 2, while an isola is just a mushroom with its base “squeezed off”.

Although, normally, only the stable steady states are observed in experiments, it is possible to locate and stabilize unstable steady states. A feedback method was used by Laplante to stabilize and track the unstable steady state in the iodate—arsenite system. Ross and co-workers have used feedback techniques to stabilize unstable steady states in illuminated thermochemical systems such as the \(S_2O_6F_2\) and o-cresol-phthalein reactions as well as \(ZnSe\) interference filters. Model-independent control techniques have been recently introduced for stabilizing unstable steady and periodic states in chaotic systems (described in section VI).

While bistability is the most common form of multistability, it is possible to have more than two stable steady states. One can envision tristability arising from a quintic nonlinearity in a one-variable system, with the three stable states separated by two unstable states. Multistability is also not restricted to steady-state behavior. Birhythmicity, where two different oscillatory states are displayed over a range of operating conditions, as well as steady-state tristability, has been observed.
in experimental systems. In principle, multistability is possible between all of the various combinations of steady, oscillatory, and chaotic states, and a number of these are described in section V.

III. Oscillatory Reactions

Although oscillatory reactions have had a long history in chemical kinetics, the first definitive characterization of a chemical oscillator was put forth less than 25 years ago. Zhabotinsky’s pioneering work set the stage for the conceptual breakthrough of the Field–Körös–Noyes mechanism, a scheme that accounts for the oscillations of the BZ reaction in terms of elementary steps. Three processes were proposed as essential components of the reaction: (A) the BrO₃⁻ oxidation of Br⁻ to produce HOBr and Br₂, which subsequently brominate the organic substrate, (B) the autocatalytic generation of HBrO₂ with the concurrent oxidation of the metal catalyst, and (C) the oxidation of the organic substrate by the catalyst to regenerate Br⁻. The three processes take place successively to constitute one oscillation, and the sequence is then repeated. When Br⁻ is consumed to a critical concentration in process A, the autocatalysis in process B takes place; the Br⁻ regeneration in process C effectively “resets the clock” by returning the system to process A.

In 1974, Field and Noyes proposed their distillation of the FKN mechanism, a three-variable scheme called the Oregonator. Used extensively for modeling the BZ reaction and as a generic model for nonlinear oscillations, the Oregonator consists of five irreversible steps:

\[
\begin{align*}
A + Y &\rightarrow X + P \\
X + Y &\rightarrow 2P \\
A + X &\rightarrow 2X + 2Z \\
2X &\rightarrow A + P \\
Z &\rightarrow fY
\end{align*}
\]

where X ≡ HBrO₂, Y ≡ Br⁻, and Z ≡ Ce(IV) are the variables. The concentration of the reactant A ≡ BrO₃⁻ is held constant as is hydrogen ion concentration (absorbed into the rate constants), and the “product” P ≡ HOBr (which goes on to brominate malonic acid) does not appear in the rate equations. Because only the features essential to the dynamical behavior are included in the model, there is the appearance (in the third and fifth steps) of transmutation of the elements! A two-variable reduction of the Oregonator by Tyson and Fife is currently in wide use for describing the spatiotemporal behavior of the BZ reaction (section VII).

Many modified BZ reactions have appeared over the years, some with only minor variations and others involving major alterations. All have served as tests of the FKN mechanism. It came as a surprise that the metal ion catalyst could be eliminated altogether in systems with certain aniline or phenol derivatives as the organic substrate. These “uncatalyzed” BZ systems utilize the aromatic reactant species as a one-electron transfer agent much like the metal catalyst in the classical system. Perhaps even more surprising was the discovery of oscillatory behavior in a CSTR system containing only acidic bromate, bromide, and the metal ion catalyst. Remarkably, this system, the “minimal bromate oscillator”, was predicted in modeling studies of the inorganic subset of the FKN mechanism before its experimental discovery. Some modified BZ systems have led to questions not easily answered by the prevailing mechanistic understanding. Noszticzius carried out experiments with BZ solutions containing an excess of Ag⁺ ions such that the Br⁻ concentration is kept at very low levels. These and related experiments suggest that, for certain experimental conditions, there is an alternative “non-bromide control” mechanism for the BZ reaction.

While the Oregonator faithfully accounts for much of the behavior of the BZ reaction, the chaotic behavior of this system (discussed in section VI) defied modeling descriptions until only recently. A new scheme, based on the FKN mechanism, has been proposed by Györgyi and Field for modeling chemical chaos in the BZ reaction. This model includes bromomalonic acid as a key variable, with its effect on the regeneration of Br⁻ providing an important additional feedback source. The Györgyi and Field model, which comes in seven-, four-, and three-variable versions, generates behavior in good agreement with the experimental measurements of “low-flow rate” and “high-flow rate” chaotic behavior. It has also been used in modeling chaos control experiments with the BZ reaction.

Another oscillatory reaction, also serendipitously discovered and extensively studied over the past two decades, is the oxidation of NADH by O₂ catalyzed by horseradish peroxidase. This and related in vivo reactions are known as peroxidase–oxidase (PO) reactions. Damped oscillations were observed in the PO reaction by Yamazaki et al. in 1965, and sustained oscillations were found by Nakamura et al. in 1969. The reaction is typically carried out with methylene blue and 2,4-dichlorophenol added to enhance the oscillatory behavior. In order to conserve the peroxidase enzyme, a semiopen reactor is often used, where NADH is slowly pumped into the PO system. Strong support for this assertion has appeared in recent studies by Olsen and Larter and co-workers showing that the chaotic behavior arises via a period-doubling cascade. A number of mechanistic investigations of the PO reaction have been carried out, with the most detailed being that by Aguda and Larter. While the mechanism is complex and several important intermediate species remain unidentified, progress has
been made in clarifying the dynamic roles played by these species as well as the role of 2,4-dichlorophenol.1,43 The essential features of the reaction are reproduced remarkably well by a simple four-variable model proposed by Olsen.44 The feedback arises from two autocatalytic processes involving two radical species, one thought to be NAD* and the other denoted "compound III". While the Olsen model exhibits period-doubling cascades much like those found in the recent experimental studies, there is a need to connect the minimal model to more complete mechanistic descriptions.

The "original" oscillatory reaction, the Bray reaction,5 was perhaps an unfortunate system for inaugurating the field of nonlinear chemical dynamics. Subject to many studies over the years, its mechanism—fraught with the complexities of hydroxyl radical chemistry and interfacial transport—remains only partially understood.45 A much younger reaction, the Briggs–Rauscher46 reaction, seems an appropriate system for rounding out a discussion of the "early" chemical oscillators. Discovered by two high-school teachers, it was conceived by combining some of the reactants of two known oscillators, the BZ and Bray reactions. The result was an oscillatory reaction comprised of hydrogen peroxide, iodate, manganese(II), and malonic acid which has been used extensively in dynamical studies and has been characterized by similar reaction mechanisms in independent investigations.45 In the next section, a new phase in the study of oscillatory reactions is described: the systematic design and characterization of chemical oscillators.

IV. New Chemical Oscillators

By the late 1970s, despite considerable theoretical progress on the nature of chemical oscillation, the only known chemical oscillators were either (a) biological in origin, like the glycolytic and oxidase—peroxidase systems; (b) discovered accidentally, like the Bray and BZ reactions; or (c) variants of those in group b. None of these routes to finding oscillating reactions offered much guidance to those seeking new systems of interest, particularly systems that might lend themselves to mechanistic study. Efforts to specify necessary and sufficient conditions for chemical oscillation or to find new chemical oscillators had proved surprisingly frustrating.

An important theoretical insight was provided49 by an analysis of a simple mathematical model consisting of two "rate" equations:

\[
\frac{dx}{dt} = (-x^3 - \mu x + \lambda) - ky \\
\frac{dy}{dt} = (x - y)/\tau
\]

Equation 2 with \( k = 0 \) and appropriate choices for \( \mu \) and \( \lambda \) has one unstable and two stable steady states for \( x \); the system is bistable. The \( y \) variable provides a simple feedback that, for large enough values of the feedback parameter \( k \) and the relaxation time \( \tau \), causes the two-variable system to oscillate periodically. If we plot the behavior of the system at fixed \( \mu \) and \( \tau \) as a function of the parameters \( k \) and \( \lambda \), we obtain the characteristic "cross-shaped phase diagram" shown in Figure 3, with regions of bistability and oscillation separating regions in which only one of the steady states is stable.

The behavior illustrated in Figure 3 is seen in a number of chemical systems, particularly those containing autocatalytic reactions, when the reaction is carried out in a continuous-flow, stirred tank reactor (CSTR).50 This device, which provides the major experimental advance needed to create new chemical oscillators, offers a means of maintaining a system far from equilibrium by continuously supplying the reaction vessel with fresh reactants and allowing reacted material to leave so as to maintain constant volume.51

![Figure 3. A schematic cross-shaped phase diagram.](image)

A systematic approach to designing oscillating reactions, pioneered at Brandeis in the 1980s,52 led to the development of literally dozens of new oscillators. The technique begins with the identification of an autocatalytic reaction. Its behavior in a CSTR is then studied, and a region of bistability is sought. If such a region is found, one then seeks a feedback species, which interacts with one or more species in the bistable system in such a way as to narrow the region of bistability and on a time scale long with respect to the characteristic relaxation times of the system to its two stable steady states. This latter requirement is equivalent to choosing \( \tau \) sufficiently large in the model eqs 2 and 3, so that the system tends to follow the hysteresis loop of the bistable system except when the feedback causes it to jump from one of the steady states to the other. If an appropriate feedback species can be found, then one adds increasing amounts of that species to the input flow of the reactor until the bistable region narrows to a point and oscillatory behavior begins to set in.

Implementation of this approach led to the first systematically designed chemical oscillator, the chlorite—iodate—arsenate system.53 This discovery was soon followed by the development of many more oscillating reactions based upon the complex redox chemistry and autocatalytic reactions of the chlorite ion and related oxyhalogen species. The BZ reaction and its relatives, as well as several new systematically designed systems, constitute the bromate family of oscillators, and many additions to the Bray reaction have filled out the iodate group.

Oxyhalogen chemistry provided the backbone to the body of chemical oscillators, but by the mid-1980s, arms and legs were beginning to sprout in the form of oscillating reactions based on the chemistry of other columns of the periodic table. The first sulfur-based oscillator, the hydrogen peroxide—sulfide reaction,54 was soon joined by about half a dozen other such systems. Although the BZ reaction contains an organic species, usually malonic acid, the key chemistry leading to oscillation is really that of the inorganic reactants. The cobalt-catalyzed air oxidation of benzaldehyde55 constitutes the first nonbiological oscillator in which organic reactions play the major role. The cerium ion in the BZ reaction proved to be a prototype for the role of metals in chemical oscillators until nearly the end of the decade; metal ions, if they appeared at all, served only as catalysts. Finally, the first member of a group of oscillators
based on manganese chemistry was discovered. When it was recognized that phosphate ion plays a crucial role in stabilizing a key Mn(IV) intermediate, it became possible to design over a dozen manganese-based oscillating reactions. Another useful concept, which has aided in the design and analysis of many new oscillators, is that of pH-driven oscillators. These are systems in which the pH undergoes large oscillation and in which $[H^+]$ drives the oscillation, in the sense that oscillation ceases if the system is buffered.

Successes in designing new oscillating reactions have been accompanied by advances in the mechanistic understanding of these often complex reactions. While most early mechanistic work focused on the BZ reaction, more recent efforts have yielded a variety of elementary step mechanisms and empirical rate law models that are remarkably successful in describing the behavior of many of the new oscillators. A general mechanistic classification of oscillating reactions based on their dynamics rather than their chemistry has recently been proposed.

The availability of many new oscillating reactions and mechanisms both facilitated and made more necessary the development of a systematic means of classifying chemical oscillators into meaningful groups. This effort at chemical taxonomy was aided by the formulation of the concept of a minimal oscillator, defined as that member of a family of chemical oscillators whose components are found, as reactants or intermediates, in all members of the family. The first such oscillator to be identified was the minimal bromate oscillator, in which the bromate—iodide and chlorite—iodide oscillators are linked through the common reactant I$^-$. A sense of the rich dynamical behavior which this system of three simple inorganic ions displays can be gleaned from the dynamical phase diagram in Figure 5.

In a physically coupled system, the subsystems reside in different vessels but are linked by the physical transfer of material between them. A special case involves electrical coupling, in which current flows in or out of one subsystem as a result of the chemical changes in another subsystem. A more commonly employed configuration accomplishes the coupling by mass transfer, usually via diffusion or facilitated diffusion. Typically, the reaction occurring in each of the subsystems is the same, though this is by no means necessary.

V. Coupled Systems

A single chemical reaction, with sufficiently nonlinear kinetics, can exhibit a remarkable variety of dynamical behavior. It is natural to ask whether coupling together two or more oscillating or similarly complex reactions might lead to a still richer phenomenology. Recent research indicates that the answer is clearly in the affirmative.

The first question that must be answered in order to study coupled chemical systems is how they are to be coupled. A pair of mechanical oscillators, like springs, can easily and understandably be linked by a rigid rod or another spring. How might one link a pair of chemical oscillators? One approach is to think in terms of two types of coupling—chemical and physical.

A system of chemically coupled oscillators consists of a single vessel containing the components of two (or more) subsystems, each of which is capable of independent oscillation, that have a key species—reactant, product, or intermediate—in common. The best studied example is the bromate—chlorite—iodide reaction, in which the bromate—iodide and chlorite—iodide oscillators are linked through the common reactant I$^-$. A sense of the rich dynamical behavior which this system of three simple inorganic ions displays can be gleaned from the dynamical phase diagram in Figure 5.
Figure 5. Dynamical phase diagram of the bromate–chlorite–iodide reaction in a CSTR in the $k_N$ (flow rate) – $[I^-]_0$ plane. Fixed inflow concentrations: $[\text{BrO}_3^-]_0 = 2.5 \times 10^{-3}$ M, $[\text{ClO}_2^-]_0 = 1.0 \times 10^{-4}$ M, $[\text{H}_2\text{SO}_4]_0 = 0.75$ M. Symbols: open circles, low-frequency oscillatory state; filled circles, high-frequency oscillatory state; open triangles, low potential stationary state; filled triangles, high potential stationary state; open squares, intermediate potential stationary state. Combinations of two symbols imply bistability between the corresponding states. Reprinted from ref 64.

Figure 6. Traces of Pt electrode potential in a physically coupled BZ oscillator experiment. Bottom trace is potential V1 from reactor 1; upper trace is potential V2 from reactor 2 shifted up by 200 mV. 0–5 min: out-of-phase entrainment, coupling strength $\rho = 0.5$; 5–11 min: steady state I, $\rho = 0.75$. Coupling is switched off from 11 min to 11 min 40 s, 11.7–19.5 min: steady state II, $\rho = 0.75$; 19.5–22.5 min: steady state II, $\rho = 0.65$; 22.5–36 min: out-of-phase entrainment, $\rho = 0.56$. Reprinted from ref 68.

What sorts of behavior do coupled systems exhibit? One frequently observed phenomenon is entrainment, in which two coupled oscillators adapt their motion to one another so that they oscillate with the same frequency or with frequencies that are related by a small whole number ratio. Figure 6 shows an example of 1:1 entrainment in a physically coupled system consisting of the BZ reaction run in two CSTRs that share a common wall with an adjustable diaphragm that permits variation of the flow between the reactors, which serves as the coupling strength parameter.\textsuperscript{58}

We observe in Figure 6 that the two oscillators are entrained out of phase with one another: reactor 1 reaches a maximum in redox potential when reactor 2 is at a minimum. At a somewhat higher coupling strength, the two reactors become entrained in phase. Any pair of physically coupled oscillators must approach in-phase entrainment as the coupling approaches infinity, since in this limit the two reactors become one. More interesting, and perhaps surprising, is the fact that the system exhibits hysteresis. As the coupling strength is decreased, the in-phase mode persists through coupling strengths at which the out-of-phase mode is stable. This behavior is an example of \textit{birhythmicity}, bistability between two oscillatory states, a phenomenon that is often seen in systems of coupled oscillators. Many forms of multistability occur in chemically coupled systems. The bromate–chlorite–iodide reaction exhibits birhythmicity between two oscillatory modes, each of which resembles in wave form and mean potential the oscillations seen in one of the component systems.\textsuperscript{64} The chlorite–iodide–arsenite–iodate reaction shows tristability among three steady states in a CSTR,\textsuperscript{69} while the chlorite–thiosulfate–iodide–iodine system has another kind of tristability involving one oscillatory and two stationary states.\textsuperscript{70}

In addition to birhythmicity, two different modes of oscillation can interact in such a way as to give rise to \textit{compound oscillation}, in which the two wave forms merge to give a single complex periodic mode. An example of compound oscillation in the bromate–chlorite–iodide chemically coupled system is shown in Figure 7. Under these particular conditions, as the flow rate is changed from a region where only one mode of oscillation exists to a region where only the other mode is stable, instead of either a sharp transition between modes or a coexistence (birhythmicity) of the two, the limit cycles merge to form a single large-amplitude oscillation that has characteristics of both oscillatory subsystems.

Two other phenomena that occur in coupled oscillators are worthy of note. Oscillator death is the term given to a transition to stationary behavior when two oscillators are linked together. An example is shown in Figure 6 when the coupling, measured as the ratio of the flow between reactors to the flow through each reactor, is set at $\rho = 0.75$. Even though each reactor would oscillate in the absence of coupling, the coupled system reaches a stable steady state in which one reactor is at a high potential and the other at a low one. By turning off the coupling for about half a period of oscillation for the uncoupled system, we cause the system to travel halfway around its orbit and to become locked in a complementary steady state when the coupling is reinstated.

Just as coupling can cause oscillators to cease oscillating, it can induce oscillation in systems that show only steady state behavior when uncoupled. This phenomenon is known as \textit{rhythmosogenesis} and was first demonstrated experimentally in the chlorite–iodide reaction by Boukalouch et al.,\textsuperscript{71} who physically coupled two CSTRs containing the system in the reduced and oxidized steady states and observed periodic oscillation in both subsystems at appropriate values of the coupling strength.

Although we have focused on results for pairs of coupled subsystems, it is possible to study coupled systems with larger numbers of elements. Laplante and Erneux\textsuperscript{52} have studied the propagation of the transition between bistable steady states in the chlorite–iodide reaction in a system of 16 linearly coupled CSTRs. More recently, a system of eight of these units has...
been used to perform simple pattern recognition tasks. Understanding the behavior of large arrays of coupled nonlinear dynamical systems has implications for a variety of problems ranging from neural networks to the synchronization of flashing fireflies to the behavior of coupled Josephson junctions. The biological implications are particularly significant, since the caricature of a living system as a collection of coupled nonlinear chemical oscillators contains a great deal of truth.

VI. Chemical Chaos

Deterministic chaos has attracted widespread interest in the physical and biological sciences over the past two decades. It represents one of the three fundamental classes of dynamical behavior (stationary, periodic, and chaotic) and, hence, is of central importance in characterizing dynamical systems. Chemical systems have played a crucial role in the study of chaos, with the discovery and characterization of chemical chaos providing some of the most convincing—and spectacular—evidence for this important class of behavior. We will focus on low-dimensional chaos and associated complex periodic oscillations found in well-stirred chemical systems.

Oscillatory reactions carried out in CSTRs display a myriad of responses as a control parameter is varied. Bifurcations mark the qualitative changes in dynamical behavior, such as a transition from steady state to oscillatory behavior or from one type of oscillations to another, and bifurcation diagrams (plots of response vs control parameter) give a summary of the dynamics of a system. Bifurcation diagrams for oscillatory reactions typically display steady state behavior giving way to oscillations followed by a return to steady state behavior. In the oscillatory region, an intricate sequence of increasingly complex oscillations may occur, culminating in the appearance of chaotic behavior.

Studies of the BZ reaction by Roux and co-workers revealed a classic period-doubling sequence leading to chaotic behavior. This route to chaos involves successive bifurcations, each giving an oscillatory pattern with twice the period of its predecessor. Each bifurcation occurs increasingly close to the previous one, until a point is reached where the period is infinite and, hence, the oscillations aperiodic. In addition to aperiodicity, chaotic systems also exhibit extreme sensitivity to initial conditions, where two systems that differ even infinitesimally in their initial conditions evolve in time so as to diverge exponentially from one another.

Other studies of the BZ reaction by Hudson and co-workers found chaotic behavior interspersed in sequences of mixed-mode oscillations. This oscillatory behavior is characterized by a mixture of small- and large-amplitude oscillations within a cycle, and a progression of patterns is observed as a control parameter is varied. A pattern made up of one large and one small oscillation, for example, will abruptly give way to a pattern with one large and two small oscillations. This pattern is then replaced by one large and three small oscillations, and so on. Aperiodic mixtures of mixed-mode states at the transition from one state to the next were found and characterized as deterministic chaos according to a variety of diagnostics.

The characterization of chaos in the BZ reaction relied on the tools of dynamical systems theory and was not dependent on any particular model description. Nonetheless, there have been many attempts to model the behavior with various modifications of the Oregonator. One “extended” Oregonator did a good job of reproducing the mixed-mode oscillations observed by Hudson, but no evidence of chaotic behavior between the mixed-mode states could be found. An intricate sequence of patterns involving the mixing of parent mixed-mode states according to Farey arithmetic was also revealed in good agreement with the “Farey tree” found in the BZ reaction by Maselko and Swinney. Another modified Oregonator was proposed in which the stoichiometric factor in the model was parametrized to be a function of P. This scheme did a good job of simulating “bursting patterns”, a form of mixed-mode oscillations observed in the BZ reaction and in nerve impulse propagation. However, no chaotic behavior could be found in this model either. The definitive experimental evidence for chaos in the BZ reaction and the decided lack thereof in various “realistic” chemical models became the source of some controversy over the years. The paradox was resolved in 1991 by the model of Györgyi and Field, described in section III. Although quantitative agreement is still not at hand, there is currently excellent qualitative agreement between experiment and theory on chemical chaos in the BZ reaction. Recent theoretical studies have also clarified the relationship between period-doubling cascades and mixed-mode states, following earlier analyses of discrete maps.

A small but growing number of chemical systems are now known to exhibit chaotic behavior. The PO reaction has been extensively investigated over the years. Recent studies have identified not only a period-doubling route to chaos but also unstable periodic orbits in the chaotic attractor of the system. Quasiperiodicity has also been found, confirming earlier modeling predictions of this behavior, as well as chaos arising from period-doubling cascades of mixed-mode states. Other systems exhibiting chaotic behavior include the chlorite—thiosulfate reaction and the cobalt/manganese/bromide-catalyzed autoxidations of p-xylene and cyclohexanone. Although chaos is usually studied in open systems, several recent investigations have demonstrated that transient chaos may occur in closed systems where the changing composition of the system as reactants are consumed serves as the bifurcation parameter. Compelling evidence for period-doubling cascades, quasiperiodicity, and transient chaos in the closed BZ system has been presented, lending support to very early reports of possible chaotic behavior in the batch reaction. The observations are also supported by recent theoretical studies of transient chaos.

Electrochemistry has been a very fruitful area for the study of chaotic dynamics. The convenient time scales and high signal-to-noise ratios of electrochemical oscillators offer significant advantages for the collection and treatment of data. Many of the studies of electrochemical chaos have utilized metal electrodissolution reactions. Hudson and Bassett have carried out a series of investigations of the electrodissolution of copper in NaCl and H2SO4 in which a number of routes to chaos were demonstrated, such as period doubling and intermittency, Shil’nikov chaos, and quasiperiodicity to chaos on a broken torus. The electrodissolution of copper in H3PO4 has been studied by Schell and Albahadily in which simple period doubling as well as period doubling of mixed-mode oscillations was found. Complex oscillations and chaos have been studied in many other types of electrochemical processes. One system that is particularly well characterized is the reduction of In(III) at a hanging mercury electrode in solutions containing thiocyanate ion. Experimental studies by Koper et al. have characterized the mixed-mode and chaotic oscillations found in this system, and Koper and Gaspard have developed a three-variable model that reproduces many of the dynamical features. Studies of the electrocatalytic oxidations of formaldehyde, formic acid, and various alcohols have also yielded...
information about mixed-mode, quasiperiodic, and chaotic behavior. An intriguing notion advanced by Schell and co-workers is that cyclic voltammograms can be viewed as parametrically forced oscillators, with the accompanying complex periodic and chaotic oscillations. On varying the upper potential limit, scans with 2, 3, 4, etc. nonrepeating cycles are observed as well as aperiodic cycles.

New techniques for manipulating dynamical systems, originating with the Ott–Grebogi–Yorke (OGY) method for controlling chaos, have stimulated a flurry of experimental applications. The OGY method provides a simple means for stabilizing unstable periodic states by supplying tiny but precise perturbations to the system. A chaotic attractor is made up of an infinite number of unstable periodic orbits, each saddelike in character (in low-dimensional systems). It is straightforward to perturb the system in such a way that it relaxes in the attracting direction of the saddle, thus stabilizing the periodic state when such perturbations are repeated each cycle. The OGY method has been applied to a wide range of dynamical systems, with unstable periodic orbits stabilized in magnetoelastic strips, electronic circuits, and laser systems.

A reduction of the OGY method based on a map description can be used for stabilizing low-dimensional systems. Most of the experimental applications of control have used some form of this reduction, usually as simple proportional feedback. The map-based method was used for controlling chaos in the BZ reaction, in which the regular oscillations of the period-1 and period-2 orbits were stabilized out of the chaotic behavior. Figure 8 shows bromide electrode measurements of the stabilized period-2 limit cycle embedded in the chaotic attractor. Periodic states in a chaotic electrochemical system have been stabilized by Rollins and co-workers using a recursive extension of the proportional feedback method. Hjelmfelt and Ross stabilized unstable steady states in the oscillatory chloride–iodide reaction, where a control parameter was proportionally varied relative to a particular species concentration. A continuous feedback method proposed by Pyragas has also been used to stabilize periodic oscillations in the BZ reaction.

Feedback methods can be used not only to stabilize unstable states but also to track these states as operating conditions change. By combining the map-based stabilization algorithm with a stability analysis subroutine, the locus of an unstable steady or periodic state can be determined as a function of the control parameter. This hybrid method has been used to track unstable orbits in the BZ reaction through a period-doubling sequence. As in the previous methods, only tiny perturbations to the system are necessary to stabilize the states, and these states are therefore representative of the original autonomous system. Tracking also allows the stabilization of unstable states outside the chaotic regime, such as the unstable period-1 orbit in the stable period-2 regime. A particular unstable state can be followed through a complete bifurcation sequence—from the point it becomes unstable to the point it regains stability.

Stabilizing and tracking states with more than one unstable direction remains an important challenge. Such states are common in spatially extended systems, and techniques beyond those developed for low-dimensional systems are required for controlling spatiotemporal chaos. A general method for stabilizing and characterizing states with many unstable degrees of freedom has recently been proposed, where an explicit connection is made between phase space approaches, such as the OGY method, and classical linear control theory. The algorithm has been used to stabilize and characterize an unstable state found to have six unstable and three stable degrees of freedom. The method has also been used for stabilizing and tracking unstable Turing patterns through spatiotemporal chaos. When coupled with the tracking technique, the stabilization algorithm provides a model-independent continuation method for bifurcation analyses of experimental systems, similar in capability to the continuation method AUTO for model systems.

Figure 8. Stabilized period-2 limit cycle embedded in the strange attractor of the Belousov–Zhabotinsky reaction. Scattered blue points show chaotic trajectory in time-delay phase space; solid red curve shows period-2 limit cycle stabilized by using a map-based control algorithm. Measurements represent the potential of a bromide ion selective electrode. Reprinted with permission from ref 36. Copyright 1993 Macmillan.

VII. Chemical Waves

Propagating fronts are ubiquitous in nature—just imagine expanding bacteria colonies, advancing regions of metal corrosion, or infectious diseases spreading through populations. Many types of fronts, even those involving populations of microorganisms or individuals, can be formulated in terms of reaction–diffusion processes. Propagating reaction–diffusion fronts, found in many autocatalytic and oscillatory reactions, serve as ideal model systems for such processes. Fronts typically propagate with a constant velocity and wave form, converting reactants that lie ahead into products which are left behind. The bulk of the chemical reaction occurs within a narrow reaction zone, similar to a propagating flame—but with no heat.

Reaction–diffusion fronts with quadratic nonlinearities have a long history, first formally studied in 1937 by Fisher and, independently, by Kolmogorov et al. Quadratic fronts described by the Fisher–Kolmogorov equation have been the prototype over the years for propagating reaction–diffusion waves. It is now known, however, that quadratic nonlinearities cannot account for some features of propagating fronts, and cubic or higher-order nonlinearities are sometimes essential. Insights into the similarities and differences of the quadratic and cubic forms can be gained by examining the mixed-order reaction–diffusion equation. An important difference is that the cubic form yields an analytical solution for wave speed and concentration profile, while no analytical solution is known for the quadratic form. Fronts in the iodate–arsenite system, arising primarily from cubic autocatalysis, can be described in terms of an analytical solution of the corresponding reaction–diffusion equation.

Many autocatalytic reactions are now known to support propagating fronts, and several have been characterized in terms of their reaction–diffusion equations. Fronts in the ferroin—
Fe(II) and ferroin have also been characterized, where, again, the reaction onset has been characterized. Recent studies of convective convection, and some of the nonlinear behavior following the iodate--diffusion fronts in the chlorite--iodide autocatalyst is complexed by bromate system, for example, can be described by a quadratic reaction--diffusion equation analogous to the Fisher--Kolmogorov equation. Fronts in the HNO₃ oxidations of Fe(II) and ferroin have also been characterized, where, again, the reaction--diffusion equation has a quadratic nonlinearity. Nagy and co-workers have developed a large family of front systems based on acid- and base-catalyzed autocatalytic reactions. A particularly intriguing type of front has been studied in reaction mixtures supporting RNA replication, where mutant strains of RNA compete for nucleotide monomers.

Lateral instabilities occur in cubic autocatalysis fronts when the ratio of the reactant to autocatalyst diffusivities exceeds a critical value. The patterned fronts are reminiscent of cellular flames, and remarkably complex behavior—including period doubling and chaos—is displayed at certain diffusivity ratios. An example of a four-cell front is shown in Figure 9, where the concentration profile of the autocatalyst displays distinct “peaks and valleys”. The front instability requires at least a cubic nonlinearity, and it is suppressed when there is more than a slight quadratic contribution to the rate law. Fronts in 2-D and 3-D configurations as well as extremely wide fronts with dozens of cells have been studied. The latter exhibit chaotic behavior much like the intermittency found in fluid turbulence. Experimental studies of the iodate--arsenite system in a gelled medium have shown that front instabilities occur when the iodide autocatalyst is complexed by α-cyclodextrin, which results in a reduction of its effective diffusivity.

When reactions are accompanied by significant density changes, due to either heat evolution or differences in density of the reactant and product species, convection may play an important role in front behavior. Convective effects have been studied in a number of systems, such as the HNO₃--Fe(II) and iodate--arsenite reactions, and a theory for reaction--diffusion--convection behavior, including such features as double-diffusive convection, has been advanced by Pojman et al. The iodate--arsenite reaction has been particularly useful in studies of the onset of convection. Theoretical analyses have established critical parameters for the first appearance of convection, and some of the nonlinear behavior following the onset has been characterized. Recent studies of convective fronts in the chlorite--sulfite system have revealed oscillatory velocities when an acidity gradient is imposed in the reaction mixture.

Propagating polymerization fronts have been studied by Pojman and co-workers. These are similar to propagating flames, where exothermic heat release initiates reaction ahead, but with heat sensitive free-radical initiators that trigger polymerization. Fronts based on addition polymerizations in unstirred solutions of methacrylic acid and benzoyl peroxide occur with convective instabilities that give rise to pulsing propagation and the formation of fingers. Fronts have also been studied in a solid-state system consisting of a mixture of powdered acrylamide and a free-radical initiator such as benzoyl peroxide or azobisisobutyronitrile (ABN).

Oscillatory chemical systems, such as the BZ reaction, display more complex waves known as reaction--diffusion pulses. When the reactant concentrations of an oscillatory reaction are such that the system is nonoscillatory but excitable, a small perturbation beyond some threshold causes the equivalent of an oscillation to occur. In an unstirred distributed system, the oscillation becomes a traveling concentration perturbation—a propagating pulse—which moves through the steady state reaction mixture, returning the system to that state behind the wave. Such chemical systems are examples of excitable media, which play an important role in biological contexts such as the heart muscle.

Chemical waves in excitable reaction mixtures give rise to spectacular spatiotemporal patterns. In effectively two-dimensional media, such as thin films of solution, successive waves emanate from pacemaker sources to form target patterns, like those shown in the top panel of Figure 1. When waves are broken, either mechanically or by some other means, the free ends curl up to form spirals, filling the medium with patterns like those shown in the bottom panel of Figure 1. Spiral waves rotate at a frequency determined by the characteristics of the medium.

There have been many theoretical and experimental studies of wave behavior in excitable chemical media, most involving the BZ reaction. The features of chemical waves in two-dimensional media were first illustrated in the seminal papers by Zhabotinsky. Winfree began his extensive studies of spiral waves at about the same time, and the first photos of BZ spirals were published, independently, by Winfree and Zhabotinsky in 1971. Field and Noyes showed that the wave propagation velocity is given by a Fisher--Kolmogorov description and related this to parameters of the FKN mechanism. Keener and Tyson characterized the dispersion relation for successive waves, giving the dependence of velocity on period, and wave concentration profiles were measured by Wood and Ross using a linear photodiode array.

One of the most remarkable developments to emerge from studies of excitable chemical media has been the characterization of complex spiral wave behavior. Winfree noted in an early study that the core around which the spiral rotates may not be stationary and termed this behavior “meandering”. The complex behavior of spiral waves remained uncharacterized for more than a decade until digital imaging techniques, introduced by Müller, Plesser, and Hess, allowed precision measurements of the spiral core. A number of subsequent investigations showed that, depending on the “excitability” of the medium, the tip of the spiral may trace out a simple circular path or a variety of intricate “flower” patterns. Theoretical studies paralleled the experimental developments and laid the foundations for understanding the complex dynamical behavior.

The effects of inhomogeneities on wave behavior are important in the cellular excitable media of biological systems. The most significant behavior arising from medium inhomogeneity is the spontaneous appearance of spiral waves. In homogeneous media, such as solutions of the BZ reaction, spiral waves do not appear spontaneously but must be deliberately
created, typically by either physically or chemically inducing wave breaks.\textsuperscript{11,151} Spirals may also appear with special initial conditions such as cross-field stimulation\textsuperscript{157} or wave initiation in the vulnerable refractory region of a preceding wave.\textsuperscript{158} Studies of the BZ reaction with the catalyst loaded on ion-exchange beads\textsuperscript{159} or printed on membranes in specific patterns\textsuperscript{160} have shown that interacting regions with different excitation levels give rise to the spontaneous appearance of spiral waves. This may occur at spontaneous wave initiations in the vulnerable refractory region of another wave,\textsuperscript{160} as recently shown in studies of BZ waves on catalyst-loaded Nafion membranes.\textsuperscript{161} Patterned excitable media also give rise to global anisotropy in wave propagation that reflects the local cellular geometry, such as the hexagonal waves on the checkerboard grid of triangles shown in Figure 10. Detailed studies of the effects of local inhomogeneities on global wave behavior have also been carried out with the Pt—CO system by Graham et al.,\textsuperscript{162,163} where complex boundaries and patterns were created by photolithography.

The transverse coupling of chemical waves has been studied in several different configurations. Waves on the surfaces of a ferroin-loaded Nafion membrane immersed in a BZ solution couple via transport of the autocatalyst through the membrane.\textsuperscript{164} This coupling gives rise to entrainment of the wave behavior on both membrane surfaces as well as spontaneous spiral sources. Modeling studies of transverse coupling of chemical waves have demonstrated that exceedingly complex bifurcation sequences arise, even in one-dimensional configurations.\textsuperscript{165,166} Communication between chemical waves has also been studied in layers of chromatographic medium saturated with BZ solution.\textsuperscript{167,168} In this configuration, two separate wave patterns appear, one on the top and the other on the bottom of the layer. Modeling studies have shown that a nonmonotonically excitability profile separates the top and bottom patterns, which interact to form intricate crossing wave patterns.\textsuperscript{169}

The propagation of chemical waves through precision-bore capillary tubes provides a means to directly measure the critical nucleation size in excitable media.\textsuperscript{170} A wave enters and travels through a capillary tube immersed in an BZ solution and forms a hemisphere of excited solution at the exit. When the tube diameter is greater than a critical value, the excitation serves to initiate a wave; otherwise, the excitation collapses and no wave is initiated. The critical nucleation size from such experiments is in good agreement with theoretical predictions\textsuperscript{152} and indirect measurements based on the wave velocity dependence on front curvature.\textsuperscript{171} Combinations of two or more capillary tubes can be configured into logic gates, based on input and output signals in the form of chemical waves.\textsuperscript{172} An example of an AND gate is shown in Figure 11, which is comprised of two tubes with radii slightly smaller than that corresponding to the critical nucleation radius of the chemical medium. The tubes are positioned such that two waves exiting simultaneously give rise to wave initiation, while a single wave in either tube collapses at the exit. Many other logic gates are possible, and a suitable collection could be assembled into chemical wave circuitry for computational tasks. The propagation of a single wave through a maze can form the basis of an algorithm for determining minimum-length paths.\textsuperscript{173} Optimal pathways through complex labyrinths prepared with a membrane—BZ system have been determined from time-lapse video information on chemical wave position.\textsuperscript{174} Propagating waves in excitable media provide an interesting and potentially useful alternative to traditional methods for determining optimal paths and point to possible mechanisms for self-optimization in biological systems. Ross and co-workers\textsuperscript{175} have carried out extensive theoretical studies of “chemical computers” based on reactor systems coupled by mass flow.

The oxidation of CO on single-crystal Pt has proven to be an extraordinarily rich system for studies of spatiotemporal behavior.\textsuperscript{176} The surface-catalyzed oxidation takes place with a reconstruction of the Pt surface, and the associated propagating waves give rise to target and spiral patterns.\textsuperscript{177} The wave patterns have been visualized with remarkable clarity using...
photoemission electron microscopy, which allows real-time spatial imaging.\textsuperscript{178} Several types of spatiotemporal behaviors are displayed by this system that have not been observed in other excitable media. These arise from the participation of the surface reconstruction as well as global coupling and include soliton-like waves, which appear to pass through one another, and standing waves.\textsuperscript{179}

VIII. Turing Patterns

The study of traveling chemical waves has provided striking analogues of, and some insights into, similar phenomena in other systems, particularly biological systems. There exist in living systems, as well as in geological and astronomical systems, striking stationary spatial patterns, and a great deal of recent research has focused on the study of stationary patterns in reaction–diffusion systems. The fundamental idea behind this work was formulated in 1952 by the British mathematician Alan Turing in a paper entitled “The Chemical Basis of Morphogenesis.”\textsuperscript{180} Turing showed by mathematical analysis and specific, though chemically unrealistic, models that a reaction–diffusion system can have a spatially uniform steady state that is stable to homogeneous perturbations but that allows certain spatially nonuniform perturbations to grow. The system then evolves into a stationary, patterned state, now known as a Turing pattern or Turing structure, that is stable to both homogeneous and inhomogeneous perturbations. The spatial structure, typically a set of repeating stripes or spots, possesses an intrinsic wavelength that depends only upon the kinetics and concentrations of the reaction, not upon the geometry of the system.

Turing’s ideas were widely embraced by theorists, particularly those interested in biological pattern formation,\textsuperscript{181} to account for a variety of pattern formation phenomena in systems ranging from astrophysical to economic. Despite the theoretical interest in them, Turing patterns remained experimentally elusive for nearly 40 years until De Kepper and co-workers,\textsuperscript{182} working with the chlorite–iodide–malonic acid (CIMA) reaction\textsuperscript{183} in an unstirred continuous flow gel reactor, produced striking stationary spatial patterns, and a great deal of recent work was formulated in 1952 by the British mathematician Alan Turing in a paper entitled “The Chemical Basis of Morphogenesis.”\textsuperscript{180} Turing showed by mathematical analysis and specific, though chemically unrealistic, models that a reaction–diffusion system can have a spatially uniform steady state that is stable to homogeneous perturbations but that allows certain spatially nonuniform perturbations to grow. The system then evolves into a stationary, patterned state, now known as a Turing pattern or Turing structure, that is stable to both homogeneous and inhomogeneous perturbations. The spatial structure, typically a set of repeating stripes or spots, possesses an intrinsic wavelength that depends only upon the kinetics and concentrations of the reaction, not upon the geometry of the system.

To understand how the Turing patterns arise, and why it took so long for them to be found experimentally, it is necessary to examine the problem more closely. If we consider a reaction–diffusion system with two concentration variables, we can perform a linear stability analysis to determine the conditions under which the steady state will be stable to homogeneous perturbations but unstable to inhomogeneous perturbations. Qualitatively, we find\textsuperscript{181} first that one of the species, the activator x, must increase the rate of its own production, i.e., at the steady state, adding more x causes $dx/dt$ to increase, while the inhibitor y must cause the rate of its own production to decrease. A second necessary condition is that the inhibitor must diffuse more rapidly than the activator:

$$\frac{D_y}{D_x} = r > c > 1$$ \hspace{1cm} (4)

where the necessary ratio c is determined by the kinetics constants and the steady state concentrations and is typically in the range of $6 \rightarrow 10$.

Condition 4 contains the explanation for why Turing patterns were so difficult to find experimentally. In aqueous solution, essentially all small molecules and ions have diffusion constants that lie within a factor of two of $2 \times 10^{-5}$ cm$^2$ s$^{-1}$. Thus, obtaining a sufficiently high value of $r$ is extremely difficult, perhaps impossible, in typical chemical systems.

What was it about the CIMA system that made it possible to get around this problem, and what insights can be derived from this success? The chemistry of the CIMA reaction can be summarized by three component processes and their corresponding empirical rate laws:\textsuperscript{185}

$$\text{MA} + \text{I}_2 \rightarrow \text{IMA} + \text{I}^- + \text{H}^+ \hspace{1cm} (5)$$

$$r_1 = k_{1a}[\text{MA}][\text{I}_2]/(k_{1b} + [\text{I}_2])$$

$$\text{ClO}_2^- + \text{I}^- \rightarrow \text{ClO}_2^- + 1/2\text{I}_2 \hspace{1cm} (6)$$

$$r_2 = k_2[\text{ClO}_2^-][\text{I}^-]$$

$$\text{ClO}_2^- + 4\text{I}^- + 4\text{H}^+ \rightarrow \text{Cl}^- + 2\text{I}_2 + 2\text{H}_2\text{O} \hspace{1cm} (7)$$

$$r_3 = k_{3a}[\text{ClO}_2^-][\text{I}^-][\text{H}^+] + k_{3b}[\text{ClO}_2^-][\text{I}^-]/(\alpha + [\text{I}^-]^2)$$

where IMA is monoiiodinated malonic acid, CHIC(OOH)$_2$, and $\alpha$ is a phenomenological parameter that determines the iodide concentration above which the last term in the rate law of reaction 7 becomes self-inhibitory in the reactant $\text{I}^-$. Experimental and mathematical analysis of the CIMA reaction and its cousin, the CDIMA (chlorine dioxide–iodine–malonic acid) reaction, reveals that, to a good approximation, changes in the concentrations of species other than ClO$_2^-$ and $\text{I}^-$ are relatively slow, and that the $k_{3b}$ term in reaction 7 is much smaller than the $k_{3a}$ term, so that the kinetics of the CIMA reaction are well described by the two-variable model\textsuperscript{186}

$$X \rightarrow Y \hspace{0.5cm} r_1 = k'_1, \hspace{0.5cm} r_2 = k_{1a}[\text{MA}] \hspace{1cm} (8)$$

$$X \rightarrow Y \hspace{0.5cm} r_2 = k_2'[\text{X}], \hspace{0.5cm} k_2 = k_2[\text{ClO}_2^-] \hspace{1cm} (9)$$

$$4X + Y \rightarrow Z \hspace{0.5cm} r_3 = k_3'[\text{X}][\text{Y}]/(\alpha + [\text{X}]^2), \hspace{0.5cm} k_3 = k_{3b}[\text{I}_2] \hspace{1cm} (10)$$

where $X = \text{I}^-$, the activator, and $Y = \text{ClO}_2^-$, the inhibitor. The resulting rate laws can be nondimensionalized to yield a simple two-variable model

$$du/d\tau = -u + 4uv/(1 + u^2) \hspace{1cm} (11)$$

$$dv/d\tau = b[u - uv/(1 + u^2)] \hspace{1cm} (12)$$

The model (11)–(12) can be shown to have a unique steady state, $u = a/5, v = 1 + a^2/25$, which is stable if

$$b < 3a/5 - 25/a \hspace{1cm} (13)$$

Equation 13 represents a condition on the concentrations of malonic acid, iodine, and chlorine dioxide in order for the system under flow conditions to have a stable steady state. If this condition is violated, periodic temporal oscillations occur, and no Turing patterns are possible.

If condition 13 holds, we must still satisfy condition 4 in order to obtain Turing patterns. Here, serendipity enters, as it has so often in this field. In order to increase the color contrast between the oxidized and reduced states of the CIMA system, Castets et al.\textsuperscript{182} employed starch as an indicator. The familiar silver iodide complex, the activator $\text{I}^-$, is immobile, since the iodide reacts with the starch molecules as being dispersed randomly throughout the gel, the diffusion of the activator iodide ions resembles a random walk through a medium strewn with...
traps into which an iodide ion can fall and remain until the complex breaks up. The net result is that the effective diffusion rate of I$^-$ decreases significantly, by a factor that depends upon the concentration of starch and the stability constant of the complex. The starch thus provides a way of making iodide diffuse significantly slower than chlorite, satisfying condition 4, and making possible the emergence of Turing patterns. Typical patterns are shown in Figure 12.

The above qualitative argument can be made more rigorous and generalized into an approach for designing other systems that can exhibit Turing patterns.\(^{187}\) If one has an activator–inhibitor system with a homogeneously stable steady state, one seeks a complexing agent that reversibly forms an immobile, unreactive complex with the activator. If the stability constant for complex formation is $K$ and the concentration of complexing agent is $C$, then the time scales for the evolution and diffusion of the activator and inhibitor become separated by a factor $\sigma = 1 + KC$. The composition of the steady state is unchanged, but its stability is modified. In Figure 13 we show a bifurcation diagram for the CDIMA reaction with $r$ set at the physically reasonable value of 1.5. We see that in the absence of complexation ($\sigma = 1$) the solid Hopf curve lies above the dashed Turing curve, so that as we lower $b$ by changing the reactant composition, oscillation sets in before Turing patterns can arise. When $\sigma$ is made sufficiently large, e.g., 10, Turing patterns occur in the region below the dashed and above the solid line.

The Turing patterns observed experimentally occur as a two-dimensional layer in a three-dimensional medium. Typically, different reactants are fed into the two ends of a cylindrical slab of gel, and the conditions for Turing patterns are satisfied only in a relatively thin strip parallel to the gel faces and perpendicular to the concentration gradients that are set up as a result of the input flows and diffusion of species within the gel. Detailed calculations on the model equations (11) and (12) supplemented with diffusion terms yield accurate predictions of the experimental location of the \(< 1 \text{ mm} \) thick Turing pattern layer in a gel disk 2 cm in diameter containing the ingredients of the CDIMA reaction.\(^{188}\) The results show that the conditions for (a) stability of the steady state to homogeneous perturbation and (b) instability to inhomogeneous perturbation are satisfied only in a portion of the medium so narrow as to permit only a single layer of patterns to occur. Model calculations\(^{189}\) suggest that if three-dimensional patterns were to exist, the stripes or spots that comprise them would arrange themselves in ways resembling the packing of atoms or molecules in a crystal.

The calculation of the location of Turing patterns in the gel medium also produces an estimate of the reactant concentrations in the region where Turing patterns can occur. One might think that, if this composition were established in a uniform medium, it might be possible to produce transient Turing patterns in a gradient-free, closed system. Lengyel et al.\(^{190}\) demonstrated in the CDIMA system that Turing patterns can indeed be formed in this fashion.

While most work in this area has focused on the characteristics of stationary Turing patterns, there are important dynamic questions as well. Turing\(^{180}\) actually predicted a second type of bifurcation that leads from a stable homogeneous steady state to traveling wave patterns. Evidence for its occurrence in a model chemical system has recently been found.\(^{191}\) Recent experiments\(^{192}\) on the ferrocyanide–iodate–sulfite system\(^{193}\) show the existence of a variety of stationary and traveling patterns. Perhaps most interesting is the observation that
patterns evolve by the growth, elongation, and splitting of spots in a fashion that is strikingly reminiscent of the reproduction of single-celled organisms.

**IX. Outlook**

It has been well over 150 years since chemists began to notice that chemical reactions often occur with surprising dynamical complexity. For most of this long history, however, there has been a decided resistance in the chemistry community to accepting such notions as chemical oscillations. Today, thanks to several decades of intense experimental and theoretical research activity, we know that oscillatory behavior is not only possible but, indeed, common in chemical systems—and it may well be the norm when we include the chemistry of living systems. Nonetheless, chemistry colleagues may still ask, “But is this stuff good for anything?” The answer is, emphatically, “Yes!”

Over the past two decades, nonlinear dynamics has flourished in the physical and biological sciences because it is seen to be a powerful tool for understanding complexity in nature. Chemical systems have played an important role in advancing the field because they are particularly amenable to experimental and theoretical analyses and, hence, serve as ideal model systems. Perhaps the greatest success along these lines can be found in the application of the principles of excitable media to cardiology. Studies, pioneered by Winfree, on wave behavior in the BZ reaction and other excitable media have led to an understanding of the role spiral waves play in heart maladies such as tachycardia and fibrillation. 194 It would not be an overstatement to say that these studies have resulted in a fundamental paradigm shift in cardiology.

Opportunities abound for using the principles of nonlinear chemical dynamics to better understand the dynamical behavior of living systems. Recently discovered calcium waves in the cytoplasm of frog oocytes, 185 for example, give rise to spectacular spiral behavior much like that seen in the BZ reaction. What function these waves serve is not known, nor is much known about their underlying reaction-diffusion dynamics; however, their origin undoubtedly lies in oscillatory behavior involving calcium induced calcium release. 196 Simple front-type calcium waves 197 are known to occur on the surface of oocytes in many different species following fertilization, 198 and it seems likely that intercellular spiral waves will be found in many species as well. Another exciting opportunity lies in developing an understanding of the dynamics of the cell cycle—an important oscillatory reaction, indeed! Recent studies by Tyson and Novak 199 have pinpointed key intermediate species in the “chemical” mechanism, allowing the construction of a model that generates behavior in remarkably good agreement with experimental measurements. This model might well be the beginnings of a “mathematical model of the cell”, which could provide insights into living systems in much the same spirit as mathematical modeling of highly complex systems such as the atmosphere. 200

While applications to biological systems seem to be a “natural” for future opportunities in nonlinear dynamics, it is important not to lose sight of the impact fundamental studies have had—and will have—on “core” chemistry. Studies of the Pt–CO system, 176 for example, have demonstrated that spatiotemporal behavior must be taken into account for a complete understanding of the surface-catalyzed reaction. It is likely that the behavior characterized in these studies will be applicable to many other systems involving surface catalysis, some with great practical importance. Studies of model systems in electrochemistry 101 offer equally important spinoffs, with recent studies showing that spatiotemporal behavior may also play an important role in many electrochemical processes. 201 Control techniques for stabilizing dynamical states have great potential for practical applications in chemistry. 110 These methods allow real-time manipulation of a chemical process by targeting and stabilizing desired dynamical states. Applications of control could potentially improve the performance of complex chemical manufacturing processes as well as dynamical processes in related fields such as combustion chemistry.

Perhaps the most important outcome stemming from studies of chemical oscillations, patterns, and chaos is the expansion of chemistry itself. The design and development of dozens of new oscillatory chemical reactions not only supplied dynamicians with new and different systems for characterization, but a great deal of new chemistry has been developed in the process. Oxyhalogen chemistry as well as the chemistry of sulfur, nitrogen, peroxide, manganese, and many metal ion complexes has seen enormous growth in terms of basic chemical understanding. Studies of propagating waves and pattern formation have shown how chemical reactions are transformed when they are intimately coupled with diffusion or other forms of transport. We also now know that it may be impossible to predict the future behavior of a chemical system if it contains elements of feedback appropriate for chaotic dynamics.

Studies of oscillations, patterns, and chaos in chemical systems constitute an exciting new frontier of chemistry. Still in its adolescence, the field holds enormous promise and opportunity for unraveling the chemical complexities of nature.

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**References and Notes**

(7) This view, can, of course, be contradicted simply by looking around and observing, particularly in living organisms, the many examples of chemically generated temporal and spatial pattern formation.
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