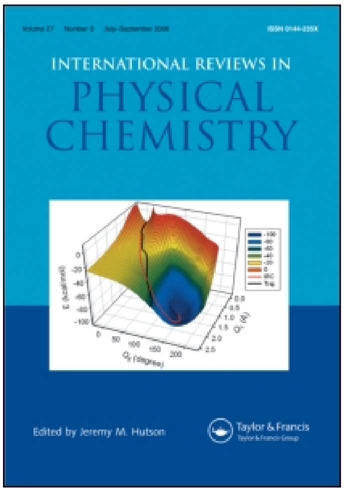

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Non-equilibrium behaviour in isothermal liquid chemical systems

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Non-equilibrium behaviour in isothermal liquid chemical systems

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This paper reviews the main features, goals, and achievements of a field of research that is now commonly referred to as 'Chemical Dynamics'. This is neither 'Molecular Dynamics', nor 'Chemical Kinetics', in the traditional sense, but rather, the study of the universal properties of time evolution and/or spatial structure of chemical systems evolving far from equilibrium.

This field has emerged over the last fifteen years. It has produced a great variety of new insights on the capability of chemical systems to organize spontaneously. It constitutes the contribution of Chemistry to the general interest that developed in practically all fields to address the question of creation of patterns and their evolution.

As indicated by the title, we shall only consider examples of liquid systems, at fixed temperature, and in homogeneous conditions. Therefore, we leave out other types of systems that may give rise to similar or related behaviours, like gas reactions, combustions, electrochemical and heterogeneous systems, or any chemical engineering processes. In fact, most of the results, definitions as well as general behaviours, can be transposed to these systems. This points out the universality of the approach.

A general overview of the field is given first and may be considered as a short version of the paper. Next, two sections are devoted to a more refined and formalized approach to temporal and spatio-temporal phenomena respectively. In both sections, experimental as well as theoretical tools are presented. Topology being an important aspect of these phenomena, we present many more pictures than equations. The article concludes with a chemical recipe that everyone should try.

1. Introduction

Over the course of a chemical reaction certain species, named reactants, are converted into other ones, labelled products. In most cases, this conversion takes place monotonically. Sometimes, however, a non-monotonic evolution may arise in a homogeneous reacting system evolving far from equilibrium; moreover, inhomogeneity may develop spontaneously. A wide range of exotic behaviours, time and/or space dependent, are thus encountered in chemical systems: periodic oscillations, chaos, hysteresis, spatial structures and chemical waves, for instance.

These unfamiliar phenomena appeared at first inconsistent with the second law of thermodynamics which, according to Boltzmann's statistical interpretation, implies maximum disorder. Nevertheless, Glansdorff and Prigogine (B 1971)† have theoretically demonstrated that thermodynamics does not rule out at all spontaneous 'organization' of an open system, provided it evolves away from equilibrium. It is only at or near equilibrium that uniformity and monotony result from thermodynamic laws, according to the minimum entropy production theorem. These authors have coined the

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† References to the separate lists of books, conference proceedings and review articles are prefixed B, C or R.

vivid phrase 'dissipative structures' for these 'ordered' behaviours, whose occurrence requires a flux of energy and/or matter. From a thermodynamic point of view, there is a sharp distinction from equilibrium structures, such as crystalline forms, with which we are familiar.

A second universal requirement comes from dynamical systems theory, and states that the dynamics must obey non-linear equations. The mass action law and the Arrhenius temperature dependence of rate constants make this condition easy to meet in chemical kinetics. However, non-linearity being a necessary but not sufficient condition, self-organization is not so widespread among reacting systems as one would perhaps expect. This can explain, at least in part, the rather late discovery of the above-mentioned non-linear dissipative phenomena.

Many areas are, in fact, concerned with non-linear behaviour developing in dissipative systems evolving out of equilibrium so that, over the years, a cross-disciplinary field of research has emerged, ranging from mathematics to biology. We emphasize that self-organization is a basic feature of the living world. In this review we restrict ourselves to a limited part of the field. We intend to deal only with liquid systems undergoing a chemical reaction whose heat release or sink is negligible. Though such a restriction may appear quite severe at first, it will rapidly be seen how substantial this area of study already is. Our aims will be to present the main results collected until now and to outline some of the problems which still remain to be solved. Since there is a huge number of papers devoted to these questions, not all of them can be cited here: no attempt is made to draw up an exhaustive survey of the literature; the references are chosen mainly for convenience.† Readers interested in other topics such as mathematics, thermodynamics, chemical engineering, biochemistry, biology, and their applications can find more specific reviews.

This article is divided into three parts. Section 2 presents a 'coarse-grained' overview of the history and phenomenology of self-organization in chemical systems. It is especially designed for those who look for a broad picture of this domain of physical chemistry. The two other parts supply a deeper insight on temporal (section 3) and spatio-temporal (section 4) behaviours, whose present stage of knowledge and understanding is summarized as simply as possible. Finally we have listed separately at the end a sample of review articles, conference proceedings and relevant monographs which provide the basis for a comprehensive approach to this domain and its related topics.

2. General overview

2.1. *Brief historical survey*

Homogeneous oscillating reactions in liquids were first discovered by chance. The earliest report seems to be due to Bray (1921) who observed an unexpected periodic decomposition of H_2O_2 in the presence of IO_3^-. Because Bray was seeking for long time-scale stability of hydrogen peroxide solutions, the importance of the fundamental problem implied by this finding escaped his attention. Nobody fully recognized its importance until the end of the sixties.

A very similar discovery was also made by accident in 1958 (or presumably in 1951) by a biochemist, Belousov (1959). He found oscillations during the catalysed oxidation

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† Despite their true importance, we do not refer to the many papers published in East European countries, in particular the Soviet Union. Indeed, except for a few of them, they are still hardly accessible (see Krinsky C 1984).

of citric acid by bromate in acidic medium. Using the redox catalyst Ce^{3+}/Ce^{4+}, one sees the solution going back and forth between yellow and colourless, a witness to the oscillating character. Later, this reaction was studied in detail by Zhabotinsky and, since 1968, by many others. It is now well known as the Belousov–Zhabotinsky (BZ) reaction.

The very existence of such homogeneous chemical oscillators remained almost unknown for a long time, and few paid attention to them. The turning point took place, seemingly, in 1968. Among the different reasons one can think of, two circumstances deserve a special mention: a meeting held in Prague (Chance *et al.* C 1973), where not only did Western scientists become aware of the BZ reaction, but also a comparison was drawn with damped oscillations observed some years before in two important metabolic pathways, namely glycolysis (Duysens and Amesz 1957) and photosynthesis (Wilson and Calvin 1955); and the Prigogine–Lefever proposal of a very simple scheme (the celebrated 'Brusselator' or 'trimolecular model'; see table 1), involving only two free species interacting in four steps, which exhibits sustained oscillations beyond a Hopf bifurcation.

Once it was realized that:

(i) thermodynamics does not at all forbid oscillations far enough from equilibrium,
(ii) oscillations might be a standard mode of metabolic process in living systems,

the real importance of chemical oscillators began to be recognized. Since that time, an impressive number of studies (theoretical, numerical and experimental) have been reported, dramatically increasing our knowledge and understanding of non-equilibrium phenomena. There is now at least one international meeting each year devoted to this field of research.

Despite very many studies, chemical oscillators still remain rather few. For historical reasons they are usually classified as halogen-based and halogen-free oscillators. The halogen families are based upon iodate (Bray 1921), bromate (Belousov 1959) and chlorite (De Kepper *et al.* 1981) chemistry. The chlorite systems were the first chemical oscillators systematically designed according to a phenomenological approach known as the 'cross-shaped phase diagram' (Boissonade and De Kepper 1980). Their discovery, which occurred only recently, proves the efficiency of a logical procedure. Halogen-free oscillators† were also found during the past three years: the air oxidation of benzaldehyde catalysed by cobalt (Jensen 1983), the methylene blue–sulphide–sulphite reaction (Burger and Field 1984) and the hydrogen peroxide–sulphide reaction (Orbán and Epstein 1985). These are the first members of a new family of sulphur-based oscillators which is currently in the way of being built up. It is worth noting that some among them give rise to oscillations in a basic medium.

Though oscillations were studied first, it must be emphasized that several other non-linear behaviours deserve an equal interest: multistability (e.g. bistationarity, birhythmicity, etc.) and its corollary, hysteresis; and deterministic chaos, that is, a seemingly erratic evolution yet describable by a few differential equations. Furthermore, not only time-dependent phenomena but also spatial self-organization of an initially uniform reacting medium is encountered. Spatial 'stationary' structures and chemical waves, first reported by Zaikin and Zhabotinsky (1970), have been extensively

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† We do not mention here the biochemical oscillators which are beyond the scope of the present paper. For a survey of oscillators in living systems see Berridge *et al.* (C 1979).

studied over the past fifteen years. Nonetheless, the interplay between reaction, convection and diffusion in these spatial chemical structures is not yet really elucidated.

Space-dependent phenomena raise several fundamental questions. Does the observed symmetry-breaking take place spontaneously or not? Is there any chemical instability at the origin of these spatial structures? Because they strongly resemble (at least in some cases) living forms, it is tempting to consider them as a possible source of morphogenesis, in agreement with the early prediction of Turing (1952). However, experimental evidence is still lacking and many difficulties will have to be overcome before reaching a clear answer.

Direct experimentation on chemical media is not the only research technique. Numerical simulations have also proved to be useful and fruitful in this field. Many 'chemical models' have been designed to this end. The simplest, proposed by Schlögl (1972), accounts for bistationarity and hysteresis. Especially designed for theoretical analysis, it involves a single independent variable X (see table 1). Yet Lotka was the first to imagine a two-variable model giving rise to damped (1910) and sustained (though marginally stable) oscillations (1920). Later on, Volterra (1931) enlarged the work of Lotka in an ecological context. Since the appearance of the Brusselator (Prigogine and Lefever 1968) many other models have been submitted to analytical and/or numerical study.

From an analytical point of view, bifurcation theory is very suitable in understanding the deterministic features of a model (Auchmuty and Nicolis 1975). On the other hand, standard stochastic analysis points out the importance of thermodynamic fluctuations near a bifurcation point. There, molecular dynamics studies confirm that long-range fluctuations may no longer obey Poisson's law as they do in general (Boissonade 1982).

Computer simulations lead to the same kind of results. Recently, special routines have become available to chemists, enabling them to determine the evolution of a homogeneous reacting system, without requiring any programming. The only thing the routine needs is the chemical scheme, written in its usual form (Gottwald 1979). Then, given a set of initial conditions and rate constants, one gets the temporal behaviour as the output, whatever the number of intermediate species (up to 20) and elementary steps. The achievement of integration procedures based on a Monte Carlo method (Hanusse 1973, Hanusse and Blanché 1981 a, b) is of great interest with respect to stochastic analysis. Indeed, they provide quantitative information on the size and amplitude of fluctuations and on their evolution. Thus, a direct comparison with theoretical predictions becomes possible.

Many efforts have been made to work out the mechanistic details of chemical oscillators. Most of them are devoted to the BZ reaction and bromate oscillators (Noyes 1980), from whence derives most of the reported experimental data. The main features of the most widely accepted chemical mechanism were proposed by Field *et al.* (1972); they are displayed in table 2 and summarized in section 2.3. A simplified version, named Oregonator (see table 1), was derived later by Field and Noyes (1974 b). Thanks to a drastic reduction in the number of independent variables (three chemical species) and steps (five elementary reactions), the Oregonator is much more fitted to tractable mathematical analysis and computer simulations. An appropriate scaling, taking into account the large differences between rate constants, can then be used to generate a simpler two-variable model (Tyson B 1976). Despite all these simplifications, it is striking to note that the model is still able to account in a semi-quantitative way for oscillations, bistability and travelling waves in the BZ reaction (Tyson 1985).

Table 1. Examples of 'chemical' models.

	Schlögl's model (Schlögl 1972)	Brusselator (Prigogine and Lefever 1968)	Oregonator (Field and Noyes 1974 b)
Model	$A+2X \rightleftarrows 3X$ $X \rightleftarrows B$	$A \rightleftarrows X$ $2X+Y \rightleftarrows 3X$ $B+X \rightleftarrows Y+D$ $X \rightleftarrows E$	$A+Y \rightleftarrows X+P$ $X+Y \rightleftarrows 2P$ $A+X \rightleftarrows 2X+2Z$ $2X \rightleftarrows A+P$ $Z \rightleftarrows hY$
Initial aim	theoretical model of bistationarity	theoretical model of stable sustained oscillations	model of the BZ reaction $X:HBrO_2$; $Y:Br^-$; $Z:Ce^{4+}$ $A:BrO_3^-$; $P:HOBr$ h: mean stoichiometric factor

Standard notations: X, Y, Z are free intermediate species whose concentrations may vary, whereas the concentrations of A, B, etc. are assumed to keep fixed values (constraints).

2.2. *Non-equilibrium phenomenology*

At this point we shall briefly review the salient features of the non-equilibrium behaviours to be discussed in this paper. Our purpose is to give the reader a flavour of the unfamiliar phenomena exhibited by certain reacting systems far from equilibrium. Accordingly, in this section, we describe bare experimental facts. Explanations, interpretations and discussions will come in sections 3 and 4.

2.2.1. *Temporal behaviours*

Let us begin with a few experimental examples of various dynamical behaviours in homogeneous uniform systems. Thus, we consider chemical reactions taking place in well-stirred open or closed reactors, excluding, for now, any diffusion process and related spatio-temporal patterns.

(*a*) *Oscillations*

In figure 1 (*a*) is presented a stable sustained oscillation such as can be obtained in a CSTR (see definition in section 2.4). Note the very regular and reproducible shape and period of the concentration–time dependence. Figure 1 (*b*) presents the Fourier transform of the time series. This type of analysis is extensively used in studying complex or chaotic behaviours. Here the perfect periodic character of the time evolution is characterized by sharp peaks at frequencies corresponding to the basic oscillation frequency and its harmonics. These harmonics simply reflect the non-sinusoidal shape of the oscillation. Depending on the quality of the experimental set-up, in particular the stability of pumping devices, the relative stability of period can be better than 1%.

In figure 2, composed oscillations are depicted. Each graph represents a time evolution. From figures 2 (*a*)–(*h*), changing the residence time in the reactor, one observes a continuous change in the steady oscillating regime, from a simple oscillation (*a*) to another (*h*) through what is called 'composed oscillations'. A succession of large and small oscillations repeats in a very regular and periodic way. Notice that, although complex, this behaviour is still purely periodic. Each sequence of composed oscillations, no matter how complex, is repeated identically.

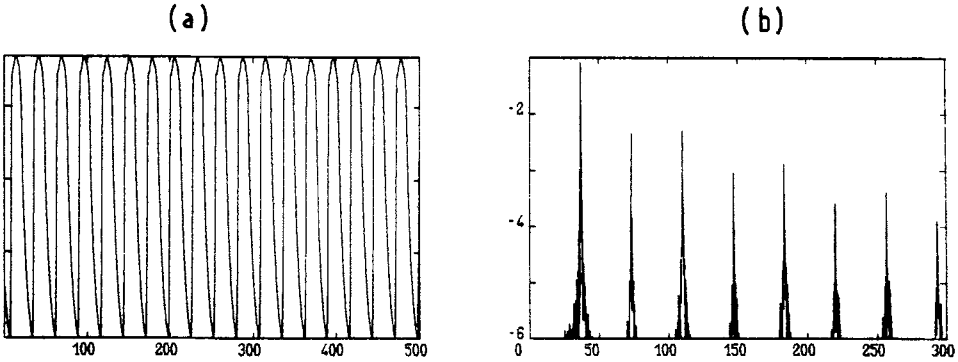

Figure 1. A periodic regime of the BZ reaction (Vidal *et al.* 1982). (*a*) Time series: Ce^{4+} concentration (a.u.) versus time (seconds). (*b*) Fourier spectrum: power spectral density (logarithmic scale) versus frequency (mHz).

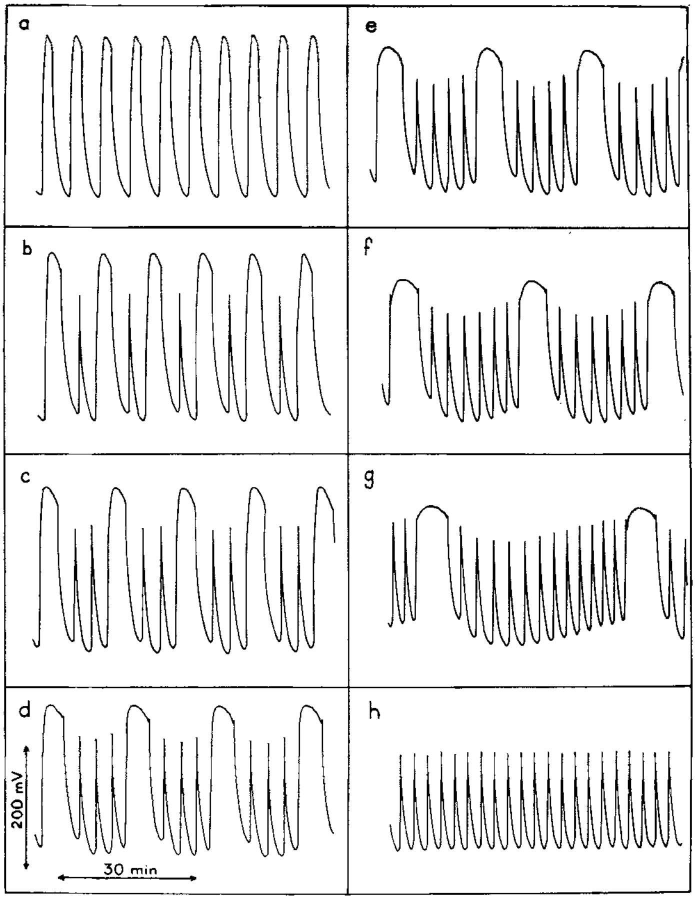

Figure 2. Time series of various composed oscillations (Epstein 1984).

(b) Bistability and birhythmicity

In figure 3 is presented a diagram which describes the dependence of steady-state concentrations as a function of a control parameter, namely the influx of species KIO_3 in the Briggs–Rauscher (1973) reaction conducted in a CSTR. This experiment shows a number of interesting phenomena. Bistability, that is, existence of two possible stable states for the same value of the control parameter, appears on the left side (states II and III). Tristability exists in the central region (states I′, II and III). On the right side, there is bistability between a steady state (state III) and an oscillating regime (state I). When two oscillating regimes coexist, one speaks of 'birhythmicity'. An example is shown in figure 4. It depicts the steady time evolution for various values of the flow rate. Two very different types of oscillating state can be obtained for the same value of the flow rate. This experiment also shows a means of forcing a transition from one state to the other, here by changing temporarily a control parameter, and revealing, or rather using, the hysteresis phenomenon associated with bistability.

(c) Deterministic chaos

Predicted by Ruelle (1973), another unfamiliar behaviour, known nowadays as 'deterministic chaos', was discovered at the end of the 70s. This refers to a seemingly erratic evolution which, in fact, is easily accounted for by a few ordinary differential equations. We have seen that, in composed oscillations, small and large amplitude variations alternate regularly. Now, for a different set of constraints, this regularity disappears: small and large amplitude oscillations are mixed at random (see figure 5) and no periodicity is detected, at least on laboratory time scales (a few hours, a day or

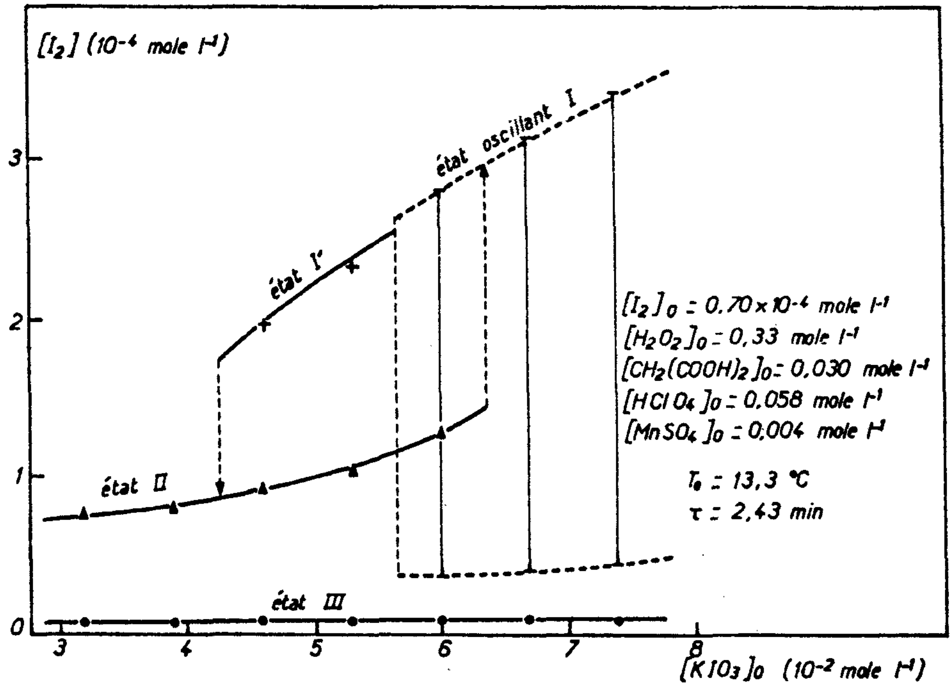

Figure 3. Experimental study of a tri-stable system (De Kepper 1978). State I undergoes a bifurcation leading to a limit cycle whose amplitude is represented by vertical bars.

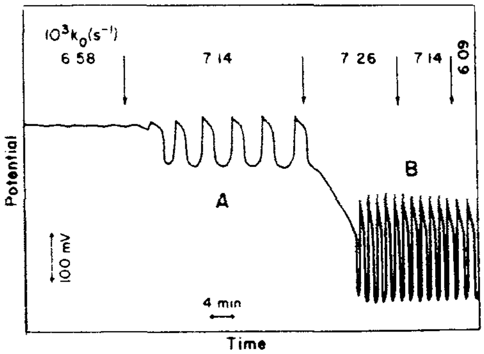

Figure 4. Birhythmicity. Forced transition from one oscillating state to the other (Alamgir and Epstein 1983).

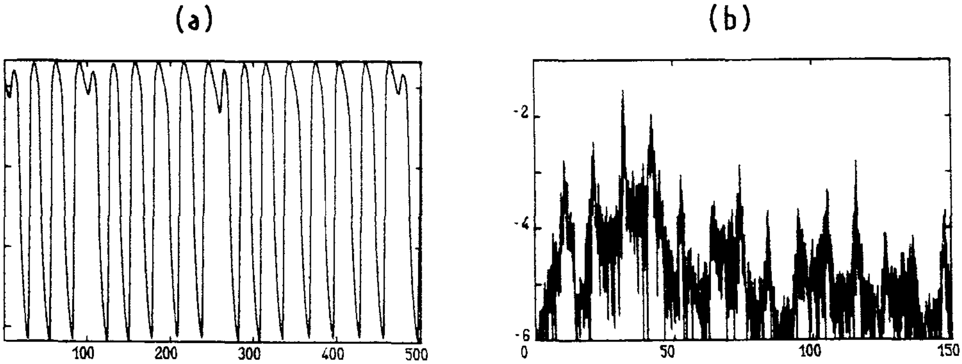

Figure 5. A non-periodic regime of the BZ reaction (Vidal *et al.* 1982). (*a*) Time series. (*b*) Fourier spectrum. Same conditions as in figure 1, except an increase of the feed flux.

so). The Fourier spectrum exhibits a 'broad band', well above the experimental noise level. In this respect, the great difference from periodic oscillations is obvious, comparing figure 5(*b*) with 1(*b*). Careful analysis has shown that the 'dwarfed' oscillations of figure 5(*a*) do reflect the chemical dynamics rather than imperfect experimentation. These observations thus provide an illustration of the mathematical concept of 'strange attractor'. Moreover the birth of such a deterministic chaos takes place through theoretically well identified 'routes' (or 'scenarios'). Figure 6 displays an example of the most famous route, i.e. the period-doubling cascade. At each step, an oscillation gives place to another one having about twice its period (sub-harmonic bifurcation). This process converges rapidly and, eventually, chaos is reached.

2.2.2. *Spatial self-organization*

In an unstirred reacting medium, spatial self-organization can take place, as discovered about twenty years ago. If an initially-homogeneous mixture is poured onto a flat surface, or into a tube, spatial uniformity may be destroyed after a while. Stationary structures and/or chemical waves emerge spontaneously in a medium left at rest. Several fundamental questions are raised by these facts, especially about symmetry breaking. But let us first have a glance at these striking phenomena.

Figure 6. First steps of a period-doubling cascade exhibited by the BZ reaction (Simoyi *et al.* 1982). The dots above each time series correspond to one period and show the doubling phenomenon due to sub-harmonic instability.

(*a*) *Spatial structures*

Bromate oscillators have been reported several times to give rise to 'stationary' patterns in shallow layers. The typical width of these structures is, say, 2–3 mm. Many different forms are obtained: spots, noodles, etc. The very nature of these patterns is not yet identified for sure. Convection is likely to have something to do with them. Neither surface effects, nor gaseous exchanges through the free surface can be disregarded.

Recently, it has been shown that a chemical oscillator is not at all necessary to generate stationary patterns. A monotonic photochemical reaction, for instance, may be used as well. Plate 1 represents an example of structures thus observed in a Pétri dish.

For the sake of simplicity, all stationary structures will, in this paper, be referred to as reaction-convection patterns.

(*b*) *Chemical waves*

Quite different from the above-mentioned structures are the chemical waves developing in an active (i.e. oscillatory or, at least, excitable) medium. Sharp, or sometimes fuzzy, concentration fronts propagate at a speed of a few millimeters per minute throughout the quiescent reacting mixture. In visible light they are easily observed with bromate reagents using the ferroin (iron-1-10-tris-phenanthronile

Plate 1. Spatial stationary pattern obtained by light irradiation of a saturated solution of mercury dithizonate. (Courtesy of Dr. J. C. Micheau.)

complex) as a redox catalyst. Red in its reduced form (Fe^{2+}), this dye turns to blue when oxidized (Fe^{3+}). In thin layers, target patterns, i.e. sets of concentric rings, propagating outwardly from a point named the 'centre', are commonplace (Plate 3). If one breaks a circular wavefront, a pair of counter-rotating spirals may then be observed. A more sophisticated perturbation of a front is even able to produce multi-armed spirals (Plate 2).

In three-dimensional devices, even more complex forms are obtained. Snapshots like that of Plate 5 are, however, difficult to take. Indeed, one has to avoid the formation by the reaction of gaseous bubbles which, moving up to the surface, would break the wavefront, thereby destroying the pattern.

Almost all the reported chemical waves are those yielded by bromate reagents. However, waves are for instance also found in chlorite–iodine–malonic acid solutions. It is nowadays generally thought that waves are an outcome of the interplay between a chemical reaction and a (convection-free) diffusion of matter. In other words, chemical waves are considered as a pure reaction-diffusion process.

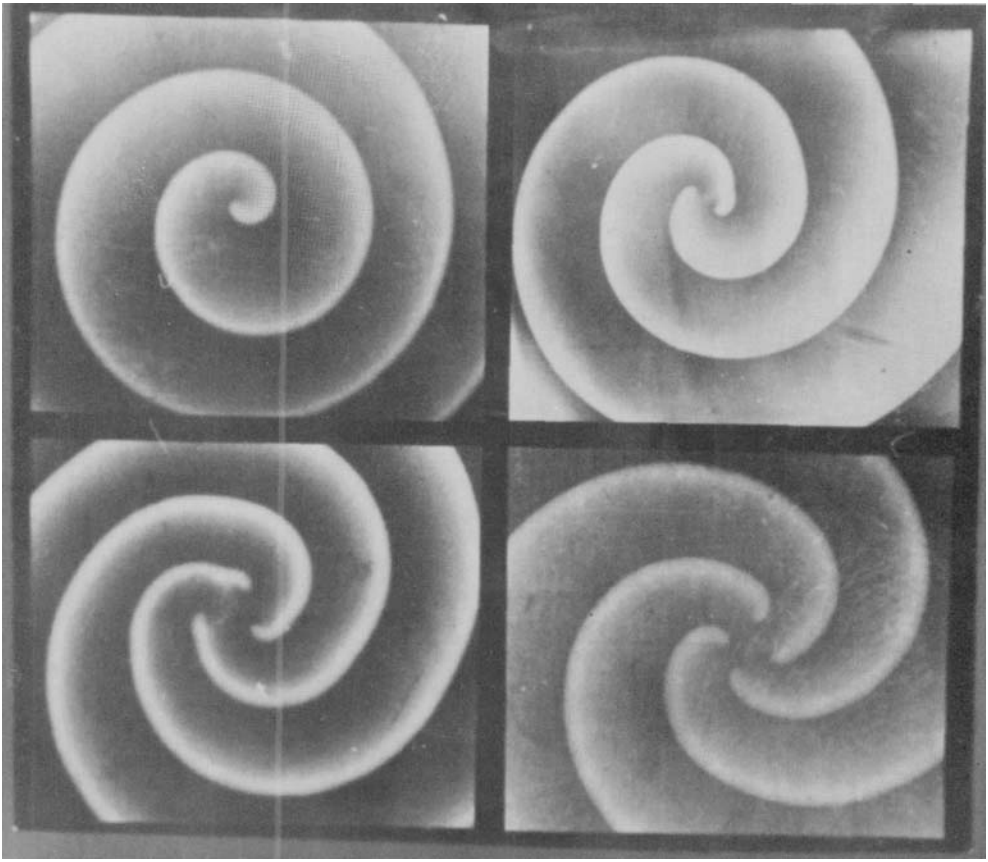

Plate 2. Multi-armed spirals observed in a thin layer of an excitable BZ reagent (Agladze and Krinsky 1982). (Courtesy of Professor V. I. Krinsky.)

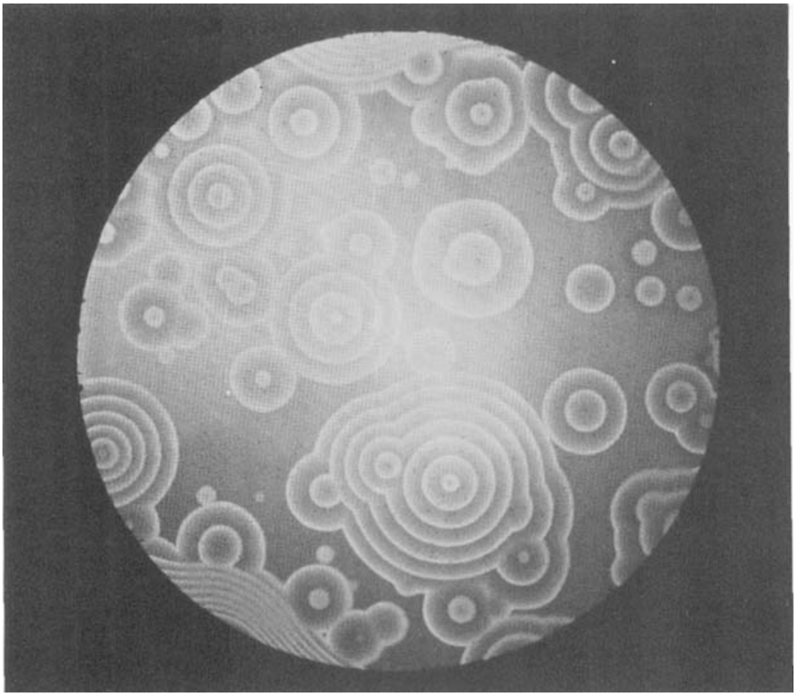

Plate 3. Two-dimensional target patterns exhibited by the BZ reaction in a layer of 1 mm depth. (Picture CNRS-CRPP.)

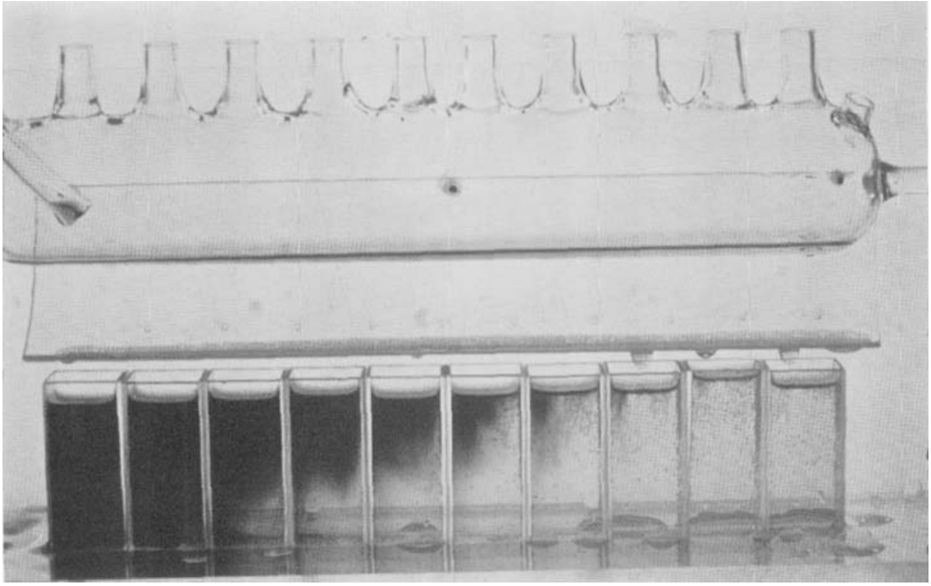

Plate 4. Pseudo-wave in a row of ten adjacent cells. The phase/frequency gradient of the Briggs–Rauscher oscillating reaction is responsible for the apparent propagation of blue (starch) fronts. (Sadoun-Goupil *et al.* 1982; Picture CNRS-CRPP.)

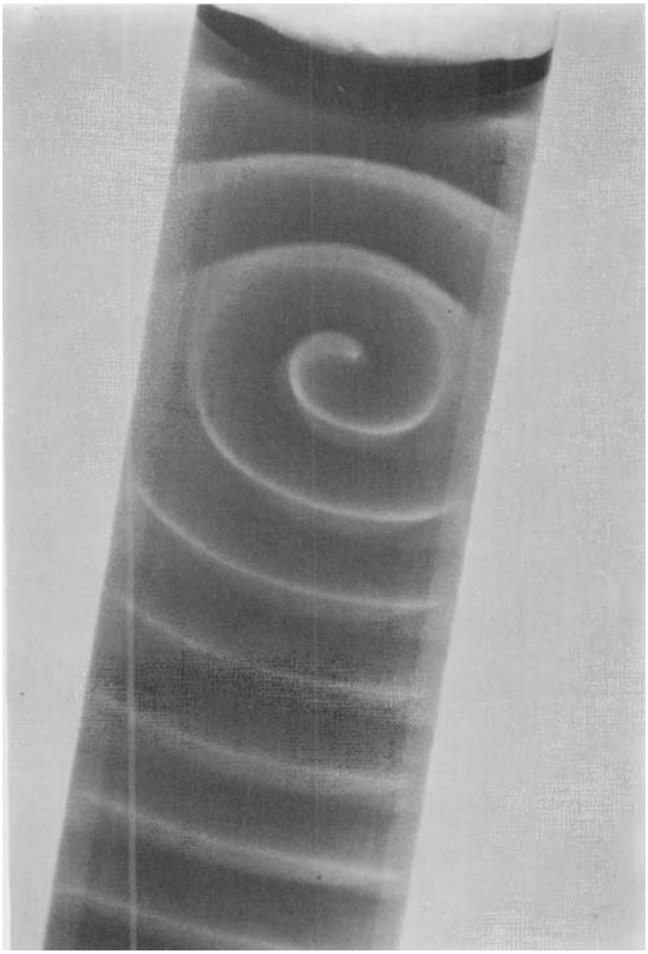

Plate 5. Three-dimensional chemical wave in the BZ reaction (Welsh *et al.* 1983). This picture appeared as the cover of a weekly issue of *Nature* in 1983, **304,** No. 5927 (Courtesy of Professor A. E. Burgess.)

2.3. *Mechanistic characterization of oscillations*

One of the major challenges is to understand the mechanism of chemical oscillators. Designing the detailed chemical mechanism of any complex reaction belongs to the most difficult tasks in chemistry. Not only can many intermediate species never be directly observed, but also rate constants often come from highly hypothetical guesses. For this reason we will not report, here, on the mechanisms of the most recently discovered oscillators, which are still in their very early stage of development. Preliminary attempts have already been made to account for the minimal chlorite–iodide oscillator (Epstein and Kustin 1985), the oscillating benzaldehyde oxidation (Roelofs *et al.* 1983), and the methylene blue–sulphide–sulphite reaction (Burger and Field 1984).

Nowadays a fairly general scheme describing how the chemistry proceeds is available for the bromate-driven oscillators (the ‘classic’, i.e. cerium-catalysed BZ reaction and its many derivatives). We will here deal only with the skeleton of this mechanism. More refined and complete discussions of the chemistry of these oscillators are given by Noyes (1980) and Field (1985).

The present description rests essentially on the proposal made by Field *et al.* (1972) for the cerium-catalysed system. This set of elementary steps, called the FKN mechanism, still provides the background of our knowledge, though it has been slightly modified and extended over the years. Basically the FKN model is based on an intrinsic bistability† involving two different processes A and B, which alternately dominate the kinetics. A third process C is responsible for the switch from B to A (see figure 7 for a schematic view).

Process A removes Br^- from the medium and produces molecular bromine according to the overall equation:

$$\text{(A)}\quad BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$

This process is assumed to involve the following sequence of two-electron redox reactions between oxybromine species:

$$\text{(R1)}\quad Br^- + HOBr + H^+ = Br_2 + H_2O$$

$$\text{(R2)}\quad Br^- + HBrO_2 + H^+ = 2HOBr$$

$$\text{(R3)}\quad Br^- + BrO_3^- + 2H^+ = HOBr + HBrO_2$$

$$A = 3(R1) + (R2) + (R3)$$

Indeed, when all reactants except the metal-ion catalyst are mixed together, one does observe for a while that the solution turns brown due to Br_2 production.

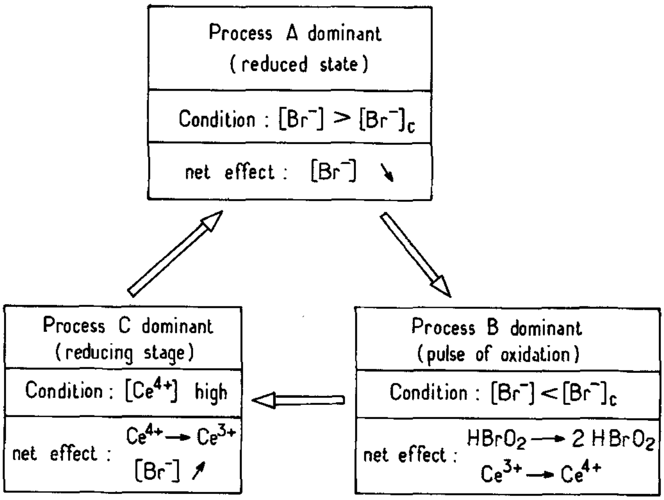

Figure 7. Simplified sketch of the FKN mechanism decomposed in three processes A, B, and C.

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† It is striking to note that the previous and independent suggestion of Zhabotinsky *et al.* (1971)–or ZZKK model—also brings into play multistationarity as the basic ingredient of oscillations.

Once Br^- concentration has been sufficiently lowered by process A, so that consumption of bromous acid by reaction R2 is very weak, process B sets in. It can be summarized as:

$$\text{(B)}\quad 4Ce^{3+} + BrO_3^- + 5H^+ = 4Ce^{4+} + HOBr + 2H_2O$$

Here is the very heart of the mechanism: that is, the single-electron oxidation of Ce^{3+} to Ce^{4+}, carried out autocatalytically by $BrO_2^{\cdot}$ (whereas the oxybromine species involved in process A have not the right potential to do that):

$$\text{(R4)}\quad 2HBrO_2 = HOBr + BrO_3^- + H^+$$

$$\text{(R5)}\quad HBrO_2 + BrO_3^- + H^+ = 2BrO_2^{\cdot} + H_2O$$

$$\text{(R6)}\quad BrO_2^{\cdot} + Ce^{3+} + H^+ = Ce^{4+} + HBrO_2$$

$$\text{(B)} = \text{(R4)} + 2\text{(R5)} + 4\text{(R6)}$$

Autocatalysis takes place through bromous acid, two molecules of $HBrO_2$ being produced by (R6) for each one consumed by (R5), while it is eventually limited by disproportionation in (R4). Experiments in flow reactors have confirmed that both A and B may actually take place under different conditions.

Now, how does the reaction go back to process A when oscillations occur? One simply needs another process C, where Ce^{4+} is a reactant regenerating Br^- (so that process B is inhibited again) and, in addition, is reduced back to Ce^{3+} (so that cerium acts as a catalyst). Such an overall process C can be written as, for instance:

$$\text{(C)}\quad 10Ce^{4+} + CH_2(COOH)_2 + BrCH(COOH)_2 + 4H_2O + 2Br_2$$
$$= 10Ce^{3+} + 5Br^- + 6CO_2 + 15H^+$$

In fact, because an organic reductant (malonic acid in this example) is involved, many different steps should be taken into consideration. The above balance equation does not reflect precisely the overall changes, but merely outlines the following: bromide ions come from brominated organic species. This point is still not completely elucidated and according to very recent experiments (Varga *et al.* 1985) using $^{82}BrCH(COOH)_2$, bromo-malonic acid would not be the source of bromide ions. Whatever these details, process C is responsible for the feedback from B to A, so that the mechanism contains a closed loop, needed to account for the oscillatory behaviour.

There is no need to say that, within an oscillating medium, the three processes develop simultaneously. Still, it is convenient to consider them separately in order to understand which concentrations oscillate rather than evolve monotonically. Rate differences between A, B and C over the course of the reaction provide the ultimate key. According to the FKN mechanism, oscillations take place as follows.

When Br^- concentration is fairly high, bromous acid stays at a low level (reaction R2), while the molecular bromine produced by (R1) reacts with malonic acid to form bromomalonic acid. Process B remains negligible because there is not enough $HBrO_2$ present to initiate the autocatalytic production of $BrO_2^{\cdot}$. However, since Br^- is consumed by process A, its concentration decreases; meanwhile, $HBrO_2$ slowly accumulates in the medium. Below some critical threshold $[Br^-]_c$, process B is no longer inhibited by reaction R2. It starts up and soon becomes dominant thanks to its autocatalytic nature. Then the high rate of Ce^{4+} production activates process C, which supplies Br^- ions more and more rapidly. Beyond $[Br^-]_c$ process B is suppressed and process A can restart. Meanwhile Ce^{4+} is reduced back to Ce^{3+}, which is thus available for a new pulse of oxidation. This whole sequence repeats itself, giving rise to oscillations. The main features of the mechanism, with respect to the three key variables Br^-, $HBrO_2$ and Ce^{4+}, are summarized in figure 7. The derivation of the simplified version named Oregonator (table 1) from this mechanism is almost straightforward (Field and Noyes 1974b, Tyson B 1976).

Oxygen effects are also well understood in the framework of the FKN mechanism. Oxygen may act very differently depending upon the reagent; either shortening the oscillation period, driving to oscillatory behaviour a medium otherwise merely excitable, or else suppressing previously existing oscillations. Nevertheless, all these effects can be explained assuming that oxygen affects only process C, whereas processes A and B remain unperturbed.

The FKN mechanism would not be complete until a full set of rate constants has been assigned to the different steps. In the list given in table 2 (Tyson 1985) several values result not from direct measurement but from difficult guesses. Among these, the rate of disproportionation of $HBrO_2$ is especially dubious. Two independent direct attempts to determine experimentally this rate constant have led to very different results (Forsterling *et al.* 1980, Noszticzius *et al.* 1983). One of them agrees with the FKN estimation, but the second is lower by a factor of 10^5. The critical bromide concentration $[Br^-]_c$ at which process B becomes dominant essentially depends on the ratio k_5/k_2, the rate of process B being driven by k_5^2/k_4. Once the value of k_4 is chosen, k_2 and k_5 can always be adjusted to fit these two ratios which are well known experimentally. Therefore, two sets of rate constants k_2, k_4, k_5 are available (see table 3) corresponding to the so-called 'Hi' and 'Lo' cases, i.e. to a rapid or to a slow rate of

Table 2. Rate constants or reactions R1 to R6 of the FKN mechanism.

Reaction	Rate constants	
R1	$k_1 = 8 \times 10^9\,M^{-2}s^{-1}$	$k_{-1} = 10^2\,s^{-1}$
R2	$k_2 = 2 \times 10^9\,M^{-2}s^{-1}$	$k_{-2} = 5 \times 10^{-5}\,M^{-1}s^{-1}$
R3	$k_3 = 2\,M^{-3}s^{-1}$	$k_{-3} = 10^4\,M^{-1}s^{-1}$
R4	$k_4 = 4 \times 10^7\,M^{-1}s^{-1}$	$k_{-4} = 2 \times 10^{-10}\,M^{-2}s^{-1}$
R5	$k_5 = 10^4\,M^{-2}s^{-1}$	$k_{-5} = 2 \times 10^7\,M^{-1}s^{-1}$
R6	$k_6 = 6 \times 10^5\,M^{-2}s^{-1}$	$k_{-6} = 5 \times 10^7\,M^{-1}s^{-1}$

Table 3. The 'Hi' and 'Lo' sets of equally plausible rate constants.

	'Lo'	'Hi'
k_2 ($M^{-2}s^{-1}$)	10^6	2×10^8
k_4 ($M^{-1}s^{-1}$)	2×10^3	4×10^8
k_5 ($M^{-2}s^{-1}$)	10	2×10^3

$HBrO_2$ disproportionation. Further studies are still required to determine which set must be rejected.†

The name 'bromate-driven oscillators' is frequently used because no substitute is known for bromate. On the contrary, both the organic reductant and the catalyst can be widely changed. Now the skeleton of the FKN mechanism is able to account for many BZ-like reactions so generated, provided suitable modifications are made. At least three situations of this type are noteworthy.

For instance, if Br^- ions cannot be produced by process C—e.g. either the catalyst is unable to oxidize the brominated organic species or, even, no such species is formed—oscillations may still occur. What is needed in that case is simply a sufficiently high concentration of molecular bromine. Indeed Br_2 hydrolysis will then produce the amount of bromide ions necessary to shift from process B to process A. It is appropriate to talk about bromine-hydrolysis-controlled (bromate) oscillators, a class to which presumably belong the reactions: Ce^{3+}–BrO_3^-–oxalic acid (Noszticzius and Bodiss 1979) and Mn^{2+}–BrO_3^-–tartronic acid (Adamcikova and Sevcik 1982).

Another rather unexpected observation was the discovery of uncatalysed bromate oscillators. As a matter of fact, many organic reductants exhibit oscillations with bromate, even though no redox catalyst is present (Kőrös and Orbán 1978, Chopin-Dumas 1981). Reaction R6, which can no longer occur in that case, should merely be replaced by a similar one involving the oxidation of an organic compound by $BrO_2^{\cdot}$ (Orbán *et al.* 1979).

Nobody will be surprised to learn that the organic reductant may in turn be suppressed in a catalysed medium. Oscillations will still be observed if bromide ions are supplied to the medium at a proper rate. This is the so-called 'minimal bromate oscillator' (BrO^{-3}–Br^-–Ce^{3+} or Mn^{2+} in a flow reactor) predicted by Bar-Eli (1981) and found soon after (Geiseler 1982, Orbán *et al.* 1982).

Much more difficult to explain within this framework are the oscillations taking place in a medium where bromide concentration is always kept at a very low level. This goal is easily achieved experimentally by adding Ag^+ to the solution in order to precipitate AgBr (Noszticzius 1979). Therefore Br^- cannot be the control species assumed by the FKN mechanism. Several possibilities are currently discussed, the search being mainly oriented towards organic and inorganic radicals, including $Br^{\cdot}$. This problem has not yet been overcome and it must be admitted that our present understanding of the question is rather poor.

2.4. *Experimental tools*

The discovery of both oscillations and spatial structures took place in a very standard manner: once the chemicals were mixed altogether in a beaker or, more generally, in a closed vessel, people merely watched the colour of the solution. It changes more or less drastically (e.g. from red to blue for the ferroin-catalysed BZ reaction), because the reaction goes back and forth between a reduced and an oxidized

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† The values appearing in table 2, which are essentially those estimated by Field *et al.* (1972) are close to the 'Hi' set. Of course, the temporal behaviour is not expected to bring any answer to this question. Fortunately, calculations show that the two sets of rate constants lead to significant differences between the profiles of waves developing in a ferroin-catalysed BZ medium. Concentration gradients should be noticeably less steep with the 'Lo' set. Thus, the answer could be an outcome of a thorough experimental investigation of waveforms.

state. Not only is this qualitative monitoring of the reaction too rough to allow for quantitative measurements but, also, conditions are such that only transients are thus observed. Indeed the system continuously drifts toward its equilibrium state, as long as there is no matter or energy input. Now, irreversible processes thermodynamics tell us that:

(i) no structure or oscillation exists at equilibrium.
(ii) equilibrium is always reached monotonically.

These are the reasons why it is necessary to keep the reacting medium away from equilibrium, so as to maintain it in a 'permanent' regime where reliable quantitative measurements may then be carried out.

When seeking for temporal behaviours, this goal is reached quite easily thanks to a constant feed of reactants (or, sometimes, of light energy (Laplante and Pottier 1982)). In order to ensure instantaneous homogeneity all over the reactor, strong mixing is required. So doing, one builds up a common device of chemical engineering: the continuously-fed stirred tank reactor (CSTR), schematically sketched in figure 8. For sake of simplicity the volume input and output flows are assumed to have the same value J, a very good approximation for all reactions we are interested in. Concentration changes inside this idealized reactor† are given by the balance equation of each species i (see notations in figure 8):

$$\frac{\mathrm{d}X_i}{\mathrm{d}t}=\dot{X}_i=F_i(X)+\mu(X_i^0-X_i) \qquad i=1,\dots,N \quad X:(X_1,\dots X_i\dots,X_N) \tag{1}$$

Total number of chemical species: N

Mean residence time: $\tau=\frac{V}{J}=\frac{1}{\mu}$

The second term, which is linear in X, simply represents the flux through the reactor, whereas the functions $F_i(X)$ account for the chemical reaction itself. According to the kinetic mass action law, these functions usually contain one or several non-linear terms,

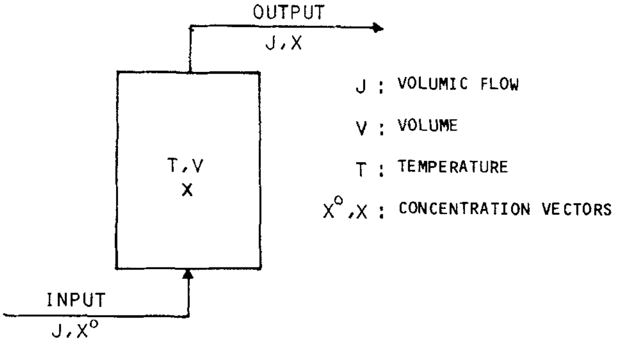

Figure 8. Schematic sketch of a CSTR.

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† The idealization lies in the fact that X components are not space dependent in (1). However, a stirring strong enough to provide a good mixing on macroscopic length scales does not necessarily make this assumption valid. It fails, in fact, each time diffusion-controlled micromixing effects have to be taken into account.

which means that (1) is a set of non-linear differential equations. Whatever the detailed expressions of the F_is, we can already draw some conclusions about the dependence of the long-time behaviour upon the magnitude of the mean residence time.

If μ is so large that any $F_i(X)$ becomes negligible compared to the linear flux term, then an obvious stationary solution is:

$$X_i^s \simeq X_i^0, \quad i=1,\ldots,N$$

Its physical meaning is trivial: when the residence time is too short, the chemical reaction cannot develop to a significant extent and one observes a mere transport of matter through the reactor. While decreasing μ from infinity, this stationary state remains stable along the 'pumped branch', down to a certain limit μ_2 (see figure 9). On the other hand, $\mu=0$ corresponds to a closed system. According to thermodynamic laws, the system goes to the equilibrium state which corresponds to the minimum of the relevant potential (e.g. Helmholtz free energy at fixed T and V). There:

$$X_i^s = X_i^e, \quad i=1,\ldots,N$$

For small, but non-zero, values of μ (i.e. of J) the system leaves equilibrium but still stays in a stationary state. Indeed the minimum entropy production theorem asserts that only one such state is stable close enough to equilibrium, along the so-called 'thermodynamic branch'. This stationary state may possibly become unstable beyond a critical threshold μ_1, thanks to the non-linear terms of F_i. It is only in between these two limits (μ_1, μ_2), when they exist and for certain chemical reactions, that fairly unfamiliar behaviours will actually take place.

Reactors used in laboratory experiments are in general made of Plexiglass or Pyrex: their volume lies between 1 and 100 ml. The feed of reactants is provided by peristaltic as well as syringe pumps, while an overflow pipe keeps the reacting volume constant. The range of explored residence times extends from a few seconds up to, say, 10^4 s. Most often the reactor is thermostated, the temperature range not exceeding 280–350 K, since we are almost always dealing with aqueous media. The transition between

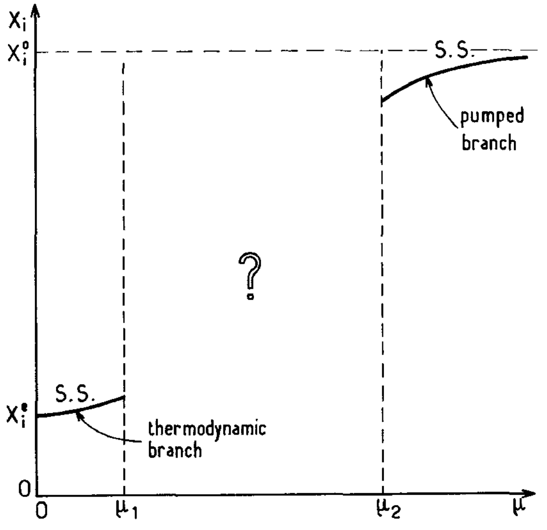

Figure 9. Dynamic features predicted by equation (1) when varying the feed flux of a CSTR.

different non-stationary regimes is usually studied by varying the volume flow J. For certain purposes, limitations result from the fact that the pumping rate cannot be scanned on a very fine mesh. Indeed, accuracy and stability of pumps is at most 0·1%. This is not fine enough for studying regimes which are stable over narrow windows of μ values.

Once a dynamical behaviour is settled in the CSTR (i.e. after decay of transients) the usual way to monitor the reaction involves either potentiometric or spectrophotometric techniques. Some other detection methods have occasionally been used, such as gas output (Bray 1921) of N.M.R. (Schluter and Weiss 1981). Both platinum reference electrodes and ion-specific (e.g. Br^- or I^-) reference electrodes† are brought into play by many experimental devices. Dissolved gas (O_2, CO_2) may also be measured with membrane selective electrodes. The time constant of the latter being fairly large, a correction must be applied to the delivered signal so as to get significant information about non-stationary states. Ion-specific electrodes have, at least in principle, the advantage of being sensitive to only one species, thus giving a signal proportional to the logarithm of a single concentration. However, the sensor is a halogen crystal, so that the response obeys Nernst's equation only over a concentration range limited by the solubility product. Furthermore, their time constant, though short ($\lesssim 1$ s), is not negligible for all purposes. On the other hand, platinum electrodes, being sensitive to the many redox reactions developing in these media, deliver a signal which depends on the concentration of several species at the same time; in short, a 'mixed' signal. This is the case too, in general, when measuring the optical density of the medium at some wavelength, since the whole absorbance is the sum of individual absorbances. However, by decomposing the absorption spectrum of the cerium-catalysed BZ reaction, it has been shown that Ce^{4+} is the only species responsible for light absorption at $\lambda = 340$–360 nm, at least at a significant level (Vidal *et al.* 1980). Therefore, spectrophotometric monitoring of this reaction at this wavelength provides a signal directly proportional to Ce^{4+} concentration.

As an example, figure 10(*a*) displays the whole set of concentration data thus collected on a BZ medium during one period of oscillation. Differentiating these time series and then subtracting the contribution due to matter flux (equation (1)) yields the overall reaction rate of production (consumption, if negative) for each measured species, as shown in figure 10(*b*). The same task can be achieved for heat release—or sink—by recording the temperature variations and monitoring the heat losses of the reactor. The BZ reaction appears to be very slightly exothermic (Lamprecht and Schaarschmidt 1978, Kőrös *et al.* 1979), heat being released only during a part of the oscillation (see figure 11; Vidal and Noyau 1980).

Spatial self-organization phenomena developing in a medium initially at rest cannot be studied in a similar way. Not only stirring but also feed flux—which implies convection coming from outside—are forbidden. The thermodynamic requirement of keeping the system at a given distance from equilibrium cannot be fulfilled, except if energy rather than matter flux is used to this end. Therefore, with the exception of photochemical processes, the experimental study of spatial structures has always dealt with transient phenomena until now. Besides, great care must be taken to prevent undesirable perturbations or effects such as, for instance, spontaneous desynchronization, hydrodynamic instabilities, and so on. In short, no standard cell or apparatus has

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† When studying the BZ system, a calomel reference electrode should not be put directly into contact with the solution because the reaction is highly sensitive to Cl^- ion.

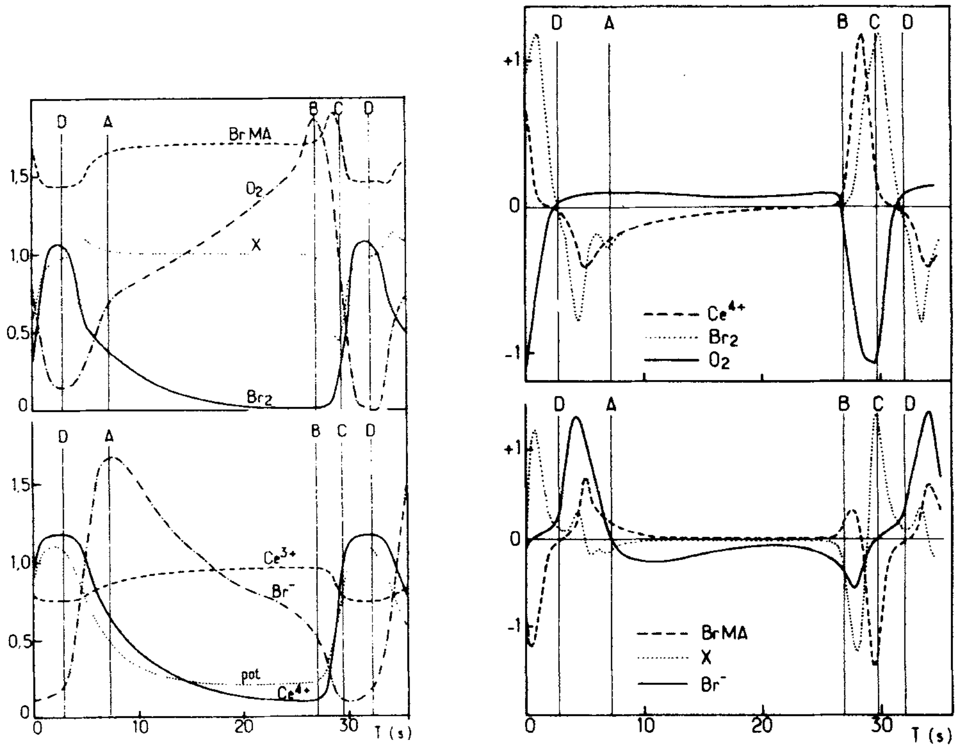

Figure 10. Oscillations of intermediate species in the BZ reaction (Vidal *et al.* 1980). (*a*) Concentration variations in the CSTR (pot, redox potential; X, unknown species). (*b*) Overall chemical reaction rates.

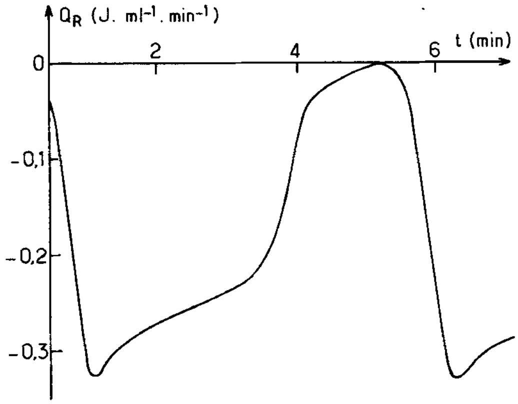

Figure 11. Typical heat release during an oscillation of the BZ reaction (Vidal and Noyau 1980).

yet been built up which would provide the right theoretical and practical conditions required, as does the CSTR in the field of temporal behaviours.

While spatial structures are not really difficult to generate under suitable conditions, their detailed quantitative analysis is far from being completed, due to these unresolved problems. Even the very nature of certain structures is hardly known and remains a matter of guess-work. Up-to-date improvements deal with the optical observation of concentration profiles (Wood and Ross 1985). Diode arrays and automatic image-processing devices allow high-resolution measurements both in space and time. Further progress is still to be expected for sure in this widely-open field of experimental research.

3. Temporal behaviour

3.1. *Definition of variables and parameters*

From the point of view of the experimentalist, all the quantities that we are concerned with, when dealing with far from equilibrium chemical dynamics, can be shown to belong to one of two distinct classes (Pacault 1978). Variables that we can control will be called constraints, or control variables, or parameters, or even bifurcation parameters, the meaning of which should become clear later. Variables that we can only observe and measure will be called responses or state variables, the value or behaviour of which is determined by the inner dynamical processes, subject to the values of the constraints. Of course, this distinction is an essential ingredient of the theoretical description. One might consider this very universal distinction even somewhat trivial. Obviously, in any physical system, given various conditions (constraints) one observes various consequences (states). It is indeed universal, but, when studying dynamical systems, the understanding and description of the structure of the relationship between external control and internal state is the central and almost unique concern that we have. Furthermore, knowledge of the topology of this relationship suffices to describe all the possible states and changes, and, for most purposes, gathers all the information that we have to know about the system. This is a consequence of the universal topological properties of dynamical systems (Abraham and Shaw 1983).

3.2. *Dynamical states and bifurcations*

The value of responses, or their type of behaviour or regime, defines the state of the system. Usually we are not interested in transient behaviours, at least to qualify a state of the system. This state will be defined rather in relation to the long-time overall behaviour. The simplest state of that kind is the stationary steady state or, simply, steady state. Others may be oscillating states, quasiperiodic states, chaotic states, etc. To acquire the status of a 'state' or 'regime', a dynamical behaviour does not need to be simple—chaos is not, as we shall see later—but it should be characterized by a few parameters. For example, an oscillation has a fixed amplitude and frequency. Sometimes it will be relevant to distinguish between various possible shapes of oscillations. But in general, a few quantitative parameters will define a state or a family of states. In most situations of interest, except the simplest, a dynamical state would be better described by the term 'regime', which is less static than 'state'.

Now, suppose that we have set up criteria to define various regimes. For a given value of the control parameters the system will be found in one particular state, or, depending on the initial conditions, in one among a few possible states, one at a time of course. Changing the constraints may then induce a qualitative change in the state of the system. At the point in constraint space where such a change occurs, we usually have what the mathematicians call a 'bifurcation', because a new regime appears, or changes stability, or exchanges stability with another one. We can keep this very loose definition of a bifurcation, or simply use the term 'change of state', and think of it very much as a change of state in a phase transition. We shall later come again to the analogy between bifurcations in dynamical systems and phase transitions (section 3.12).

3.3. *Representations and geometry of dynamics*

From what has been seen previously, the various ways that can be used to represent the information that characterizes the dynamics of a given system follows straightforwardly.

3.3.1. *Time series, evolution graph*

This is the most natural way to represent some dynamical property (see figure 12). In a given system, as many such graphs can be drawn as the number of variables. The set of constraints should be specified to understand under which conditions such a time evolution has been observed.

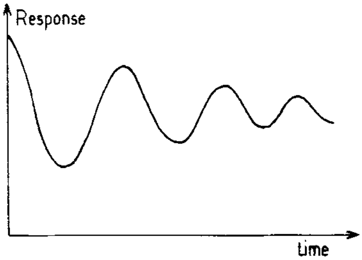

Figure 12. Time-series or evolution graph of a response or state variable. Constraints values should be specified for complete information.

3.3.2. *Trajectories, flows*

In the response space, also called phase space, we can plot the state of the system for each value of time, to obtain a trajectory that may be attracted, as in figure 13, by a limit set. This limit set may be a steady state (figure 13), a limit cycle (figure 14), or even a more complex structure (figure 15). Usually one represents projections in two or three dimensions of the trajectory in phase space. The real dimension is equal to the number of responses of the system. In chemistry, this number, usually unknown, may be very large.

The set of trajectories that can be constructed is called a flow and is said to represent a 'phase portrait'. The properties of a flow around a limit set reflect precisely those of the limit set. For instance, in figure 13 the topology of the flow is related to the presence of a 'black hole' that we call a 'sink'. These singularities of flows are precisely what we are looking for. When a bifurcation occurs, the topology of the flow changes

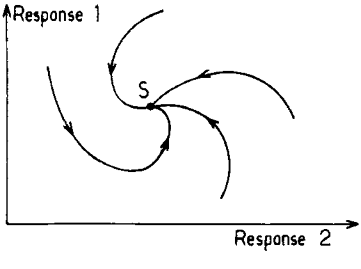

Figure 13. Trajectories in phase space or response space, also called phase portrait. The set of trajectories is called a flow. Point S is an attracting steady state (for a given set of constraints).

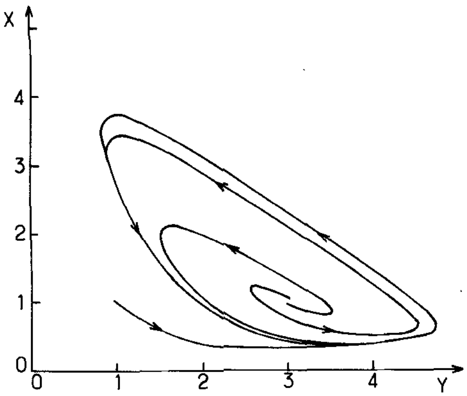

Figure 14. Limit cycle of the 'Brusselator' (see table 1). Any initial state will converge towards the closed stable orbit.

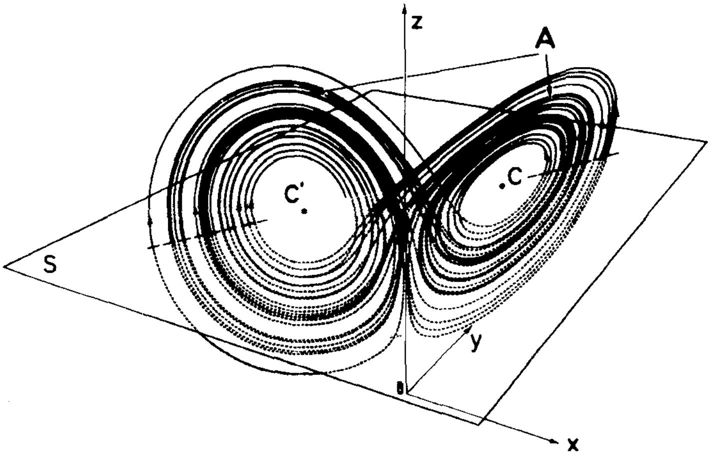

Figure 15. Strange attractor of the Lorenz model.

$$\begin{aligned}\dot{X} &= Pr(Y-X)\\ \dot{Y} &= -XZ+rX-Y, \quad Pr=10;\ b=8/3;\ r=28\\ \dot{Z} &= XY-bZ.\end{aligned}$$

qualitatively. This qualitative change is the only event that really matters, that captures the dynamical relevant property of the system. For instance, in figure 14, the limit cycle may shrink gradually as the result of changing some constraint. At some point it will disappear, leading to a flow as as shown in figure 13. At this point, a 'Hopf bifurcation' occurs.

3.3.3. *State diagram*

This diagram gathers the global information which can be obtained on a system by locating, in constraint space, the various possible states, and the lines of transition from one state to the other (figure 16). Such lines are bifurcation lines. When the transition occurs with hysteresis, two lines must be investigated, one for each direction of transition. In general, the way the transition occurs must be indicated in the state diagram. It may happen that the characteristics of transition change along a bifurcation line. It should be kept in mind that the 'real' state diagram, in particular in

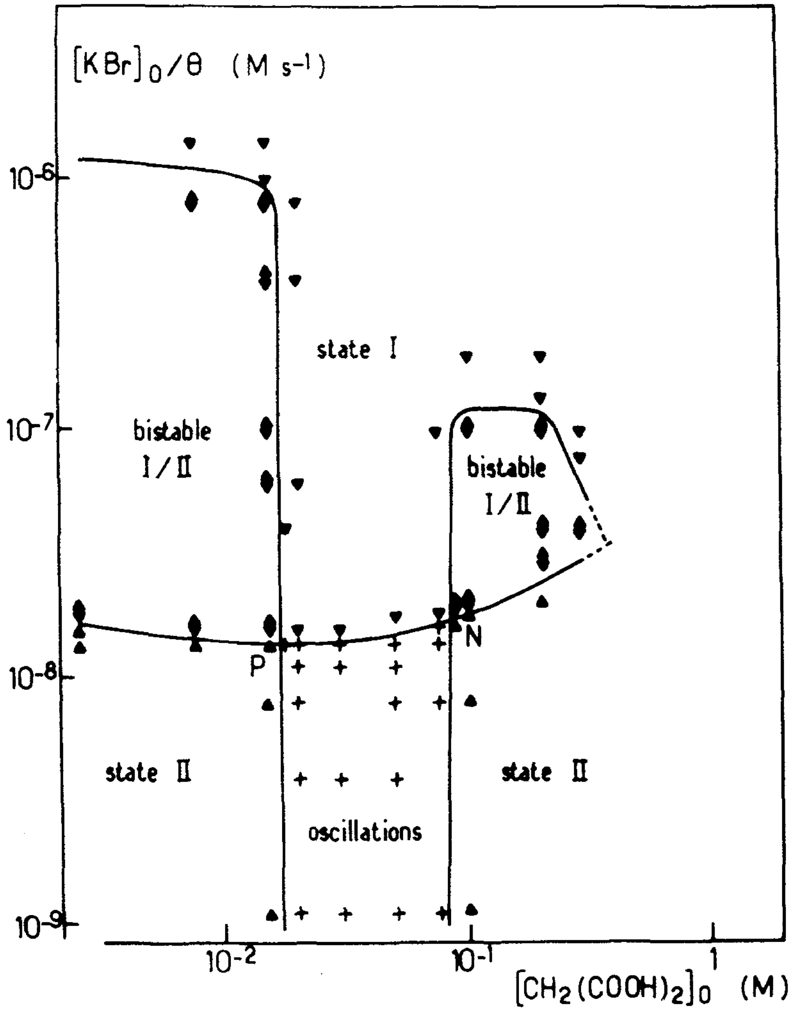

Figure 16. Experimental state diagram (Boissonade and De Kepper 1980). Notice the cross-shaped structure, appearing twice, that connects bistability and oscillation domains, a rather typical situation in chemistry.

experiments, is a high-dimensional object. One usually determines only two-dimensional sections of it. As a result, depending on how and where this section is placed, the same dynamical behaviour may appear in several separated or almost separated domains. Experimentalists have called these features 'isolas' or 'mushrooms' after the shape of the corresponding bifurcation diagram (Gray and Scott 1985). They are not a dynamical behaviour by themselves. They rather reflect the complex shape of bifurcation boundaries or of the path followed through the state diagram.

3.3.4. *Bifurcation diagram*

Such a diagram describes the dependence of steady-state features (concentration, amplitude of limit cycle, or any parameter characterizing the stationary regime) as a function of a constraint parameter. It is thus a response–constraint type of diagram. Examples follow in the next section.

3.4. *Bistability and hysteresis*

Let us now review dynamical phenomena, using the representations defined above. Bistability is one of the simplest and commonest behaviours that may be observed in a dynamical system. The corresponding bifurcation diagram appears in figure 17. In the central range of constraint values, three steady states coexist. The intermediary one is unstable, the two others are stable. For a given value of the constraint parameter, a perturbation of the response variable can force the system to jump from one state to the other. Another way to obtain this result is to sweep back and forth the constraint parameter, so revealing the hysteresis phenomenon associated to such a bistability. Now, in general, we can control several constraint parameters. One of them may control the width of the bistability region. At the very point where this width vanishes we obtain a triple steady state or critical point. We can then draw a three-dimensional bifurcation diagram, which represents the folded sheet of figure 18, a universal topology which is described by the catastrophe theory as the 'cusp catastrophe'. In some cases, as in figure 3, more than two stable states or regimes can coexist.

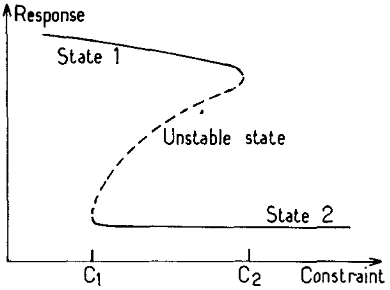

Figure 17. Bifurcation diagram. State variable, steady state or amplitude of limit cycle, as a function of a constraint. At points C_1 and C_2 a bifurcation occurs. As in all other figures, dashed lines indicate unstable steady states.

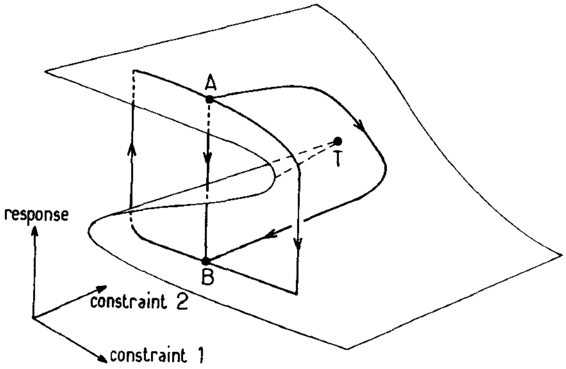

Figure 18. Universal bistability bifurcation diagram, showing three ways to reach point B, starting from point A: (i) by direct vertical transition at fixed constraints requiring an external perturbation on the response; (ii) at fixed constraint 2, by increasing constraint 1 to fall over the edge of the fold, then backing up to point B, (iii) by changing both constraints, going around triple point T. Along this path no abrupt change of the response can be detected.

3.5. *Excitability*

This is also a rather common behaviour in chemical systems. It is even more frequent in a biological context, where people have long ago studied this phenomenon, which is the basis of signal propagation in nerve membranes.

Consider a stable steady state. Let us perturb it for a very short period of time. It will relax to the steady state in a smooth, simple, possibly exponential way. When the steady state is excitable, this behaviour can be observed as long as it is perturbed below some, usually low, threshold. But if the initial transient perturbation makes the system go above this threshold, the system undergoes a large excursion in state space before returning to the steady state (figure 19). Besides, usually, the shape and duration of this excursion is independent of the initial perturbation. This appears to be an intrinsic property of the dynamics.

In figure 20 we give a topological description of this phenomenon in phase space. It is related to a very particular flow, which possesses an almost-closed orbit. Three steady states are involved, of which only one is stable. An experimental example of excitability appears in figure 21.

3.6. *Oscillations*

In figure 14 we gave an example of a 'limit cycle' which is a (here stable) closed orbit, to which converge (or from which diverge whenever unstable) all trajectories. This orbit is associated with an unstable steady state. It is important, in particular in experiments, to determine how this limit cycle appears or disappears, that is, which bifurcation is

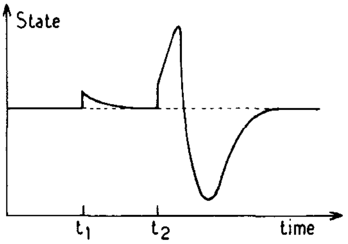

Figure 19. Relaxation to steady state in an excitable system. At time t_1 the perturbation is below threshold. At time t_2 excitability occurs.

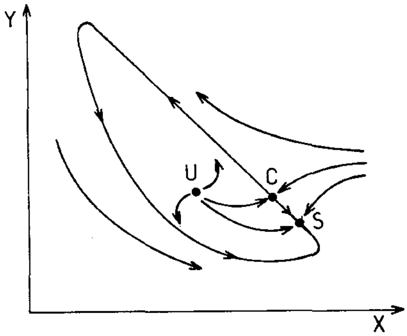

Figure 20. Phase portrait of an excitable system. Steady states U and C are unstable; steady state S is stable. When the system is pushed above the separatrix of C, instead of returning directly to S, it will loop around the 'almost limit cycle'. When C and S merge together (saddle–node bifurcation) a limit cycle is formed.

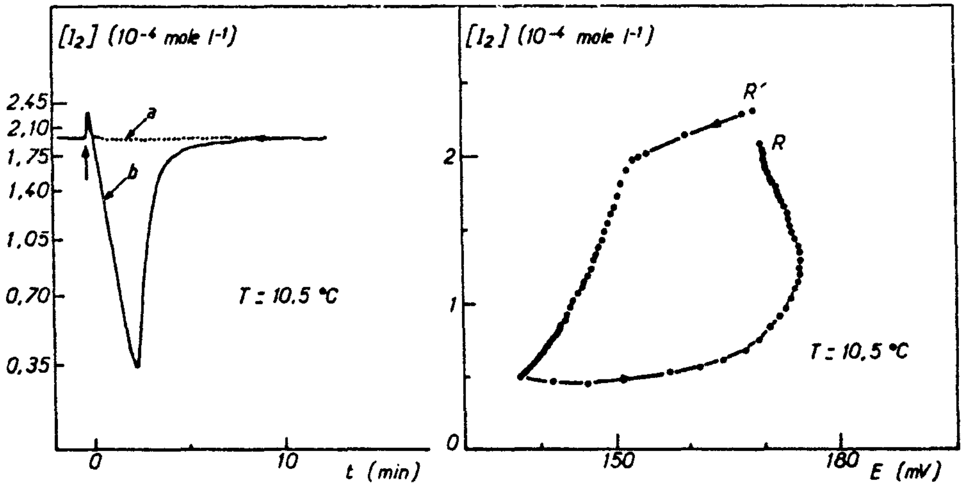

Figure 21. Experimental determination of phase space trajectory during excitability (De Kepper 1976).

responsible for its formation. We have already cited the Hopf bifurcation, which is the 'standard' way to form a limit cycle. The bifurcation diagram and phase portrait are shown in figure 22. Notice that the Hopf bifurcation itself occurs at the point where the cycle has zero amplitude. It is the principal characteristic of this transition, namely the cycle appears smoothly.

In other circumstances this may occur through a 'hard transition', immediately with a finite amplitude. One example of such a bifurcation can be deduced from figure 20. When the unstable (saddle) steady state C coalesces with the stable (node) steady state S, through what is called a saddle–node bifurcation, the 'almost-closed' orbit becomes closed. A limit cycle has appeared. The relationship between excitability and limit cycle oscillation has been observed experimentally (De Kepper 1976).

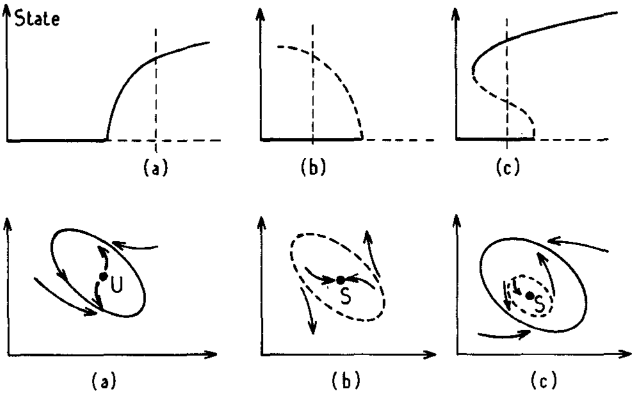

Figure 22. Schematic bifurcation diagram and phase portrait for Hopf bifurcation. (*a*) Supercritical Hopf bifurcation associated with a stable limit cycle. (*b*) Subcritical bifurcation with an unstable cycle (*c*) Generalized Hopf bifurcation. A local subcritical bifurcation is associated with a global limit cycle coalescence. Two cycles are involved, one stable, one unstable.

A third kind of limit cycle bifurcation is depicted in figure 23. It is called a saddle–loop bifurcation. Two steady states are involved, One of them is a 'source', or unstable focus, the other one is a saddle. In this bifurcation the separatrices of the saddle cross each other, forming, at the bifurcation point, what is called a homoclinic orbit, in this case a saddle–loop. These last two bifurcations, which involve several steady states at finite distance, are called global bifurcations whereas the Hopf bifurcation is a local bifurcation.

Away from the bifurcation, one usually observes 'relaxation oscillations', this name referring to the shape of the evolution graph of the concentrations, which presents fast transitions between slowly, varying states (figure 24). This particular type of oscillation, rather typical of far from equilibrium conditions, reveals the existence of some underlying bistability or rather pseudo-bistability. In fact, from this observation, a procedure for constructing a chemical oscillator has been designed and successfully applied in theoretical models (Boissonade and De Kepper 1980) as well as in an experimental context (De Kepper *et al.* 1981). A simplified recipe goes as follows: take an autocatalytic reaction; run it in a CSTR, and try to obtain a bistable system; next, find some ingredient that pushes the system to the left when in the upper branch (figure 24), and to the right when in the lower branch. If the various time scales fit nicely, you may obtain a relaxation oscillator.

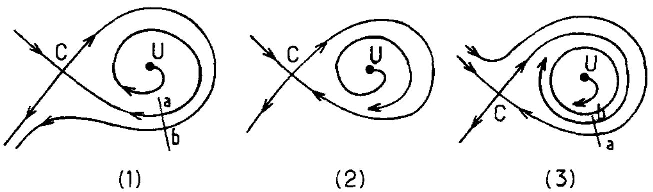

Figure 23. Saddle-loop bifurcation to a limit cycle. (1) Saddle point C and unstable focus U. (2) Saddle-loop and homoclinic orbit. (3) Saddle point C, unstable focus U and stable limit cycle. The separatrices of the saddle point C have exchanged position during the bifurcation (points a and b). Notice that the local properties of singular points do not change during this global bifurcation.

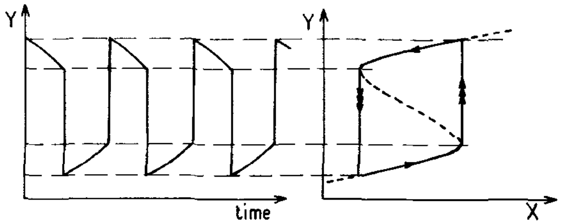

Figure 24. Relaxation oscillation and underlying pseudo-bistability. X is a slow variable, Y is a fast variable, rapidly adapting to X value. If X were fixed, a real bistability would be observed.

3.7. *Extended definition of bistability*

We shall now extend the definition of bistability to the existence of any two simultaneously stable regimes. We shall obtain in this way a number of new configurations which have been observed experimentally.

Suppose that one of the regimes is a stable limit cycle. A corresponding phase portrait in two dimensions can be easily obtained from figure 23 (3), if one adds a stable node on the lower left corner separatrix. In that case a stable node will coexist with a stable limit cycle, each of them having an attracting domain. Obviously, a bifurcation can occur on one of the branches, for instance a saddle–loop bifurcation as in the previous example, or a Hopf bifurcation as shown in figure 25 (*a*). In more complex situations, both branches may present such a bifurcation, corresponding to the coexistence of two distinct oscillations (figure 25 (*b*)). An experimental example was shown in figure 3.

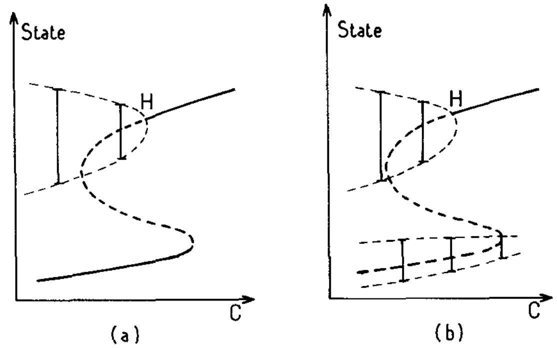

Figure 25. Extended definition of bistability. Hopf bifurcation can occur on the stable branches of a bistable system. (*a*) To the left of point H a steady state coexists with a limit cycle oscillation. (*b*) Two distinct limit cycles can coexist. This situation is referred to as birhythmicity.

3.8. *Composed oscillations*

We have already given an experimental example of this complex oscillating regime in which each period is composed of a mixing of two types of oscillations, one large and a variable number of small ones, in figure 2 (Alamgir and Epstein 1983). The geometrical representation of this phenomenon is given in figure 26. It is based on the same argument used in figure 24 to describe relaxation oscillations. In a three-dimensional phase space the trajectories lay on a folded two-dimensional sheet. This is

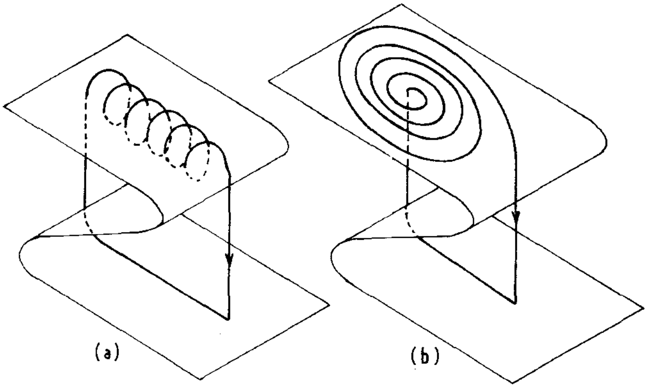

Figure 26. Two schematic representations of composed oscillations in phase-space.

the 'slow manifold'. The trajectories converge rapidly to this attracting subspace, then drift slowly on each fold of this sheet, jumping from one fold to the other. A projection in two dimensions of such a trajectory, determined experimentally, is shown in figure 27 (De Kepper 1978).

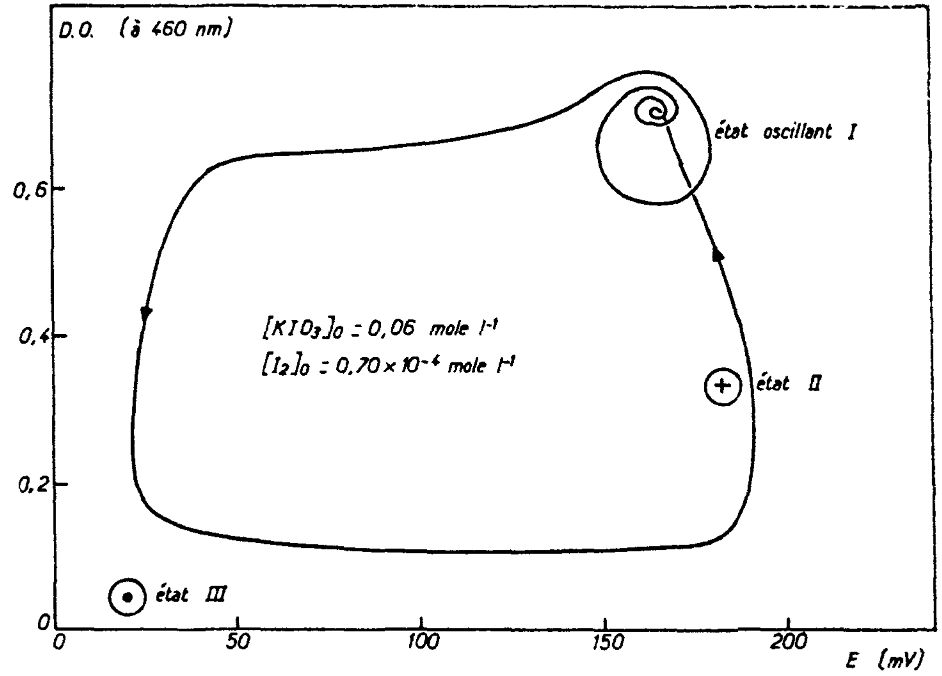

Figure 27. Experimental example of phase-space trajectory of a composed oscillation (De Kepper 1978). This is the projection in two dimensions of a trajectory of the type shown in figure 26. In this experiment, the oscillating regime coexists with two stable steady states.

3.9. *Birhythmicity*

As already seen in section 3.7, a definition of bistability extended to any kind of stable regime (figure 25 (*b*)) can explain the possible coexistence of two different oscillating regimes for the same value of the control parameters. An experimental observation was presented in figure 4 (Alamgir and Epstein 1983). From what preceeds, a geometrical representation can be constructed straightforwardly.

3.10. *Quasiperiodicity*

We now go to an even more complex behaviour in which, strictly speaking, no period can be observed. This situation may appear very close to what we have seen before. But the qualitative change that results from this lack of periodicity is crucial.

Consider figure 26 (*a*), which describes composed oscillations. Suppose that the oscillating behaviour which exists on the upper fold, also occurs on the lower fold. Without too much effort, it is possible to realize that the resulting flow has the topology of a torus. If after going through one large loop the system returns exactly to the same place, as in figure 26, the behaviour is periodic. If not, it is quasiperiodic: there is no 'phase-lock', or commensurability between the large loop duration and the small oscillation period. In experiments, it will be very difficult to distinguish between the two cases, looking only at time series. Fourier transform analysis and phase space representation will be required to detect this toroidal structure (Argoul and Roux 1985).

3.11. *Deterministic chaos*

Deterministic chaos is the most surprising dynamical behaviour that has been investigated during the last years. Chemical systems turned out to be an excellent field of experimentation for a phenomenon that remained for some time a purely mathematical subject.

Consider again figure 26(*b*) where an unstable focus lies on the upper sheet of the fold. Suppose that the reinjection to the upper sheet occurs close to this unstable focus, but in a slightly irregular position. The instability of the focus provides a mechanism for deviation amplification. The trajectories will spread over the upper sheet before falling down the edge of the fold, after a variable number of rotations. Suppose now that the trajectories gather again on the lower sheet as the result of a contracting dynamics. We might obtain a flow as depicted in figure 28. This very crude description allows us to realize that in three dimensions such a stretching, mixing, folding and contraction of flows is not in contradiction with deterministic dynamics. The resulting time series will look very irregular, although no stochasticity, in the physical sense of an unknown driving force, has to be included in the description. This very strange phenomenon deserves a more detailed discussion. It has become a field of investigation by itself in chemical dynamics, and specific methods have been designed to observe and characterize it.

Any physical system whose temporal behaviour is described by a set of non-linear differential equations (or discrete mappings as well) may give rise to such a deterministic chaos. This very important conclusion was originally pointed out by Ruelle and Takens (1971), who thus completely renewed our knowledge and understanding of turbulence phenomena. Hydrodynamics was the first experimental field to be explored, though in principle many fields are concerned. Whereas Ruelle

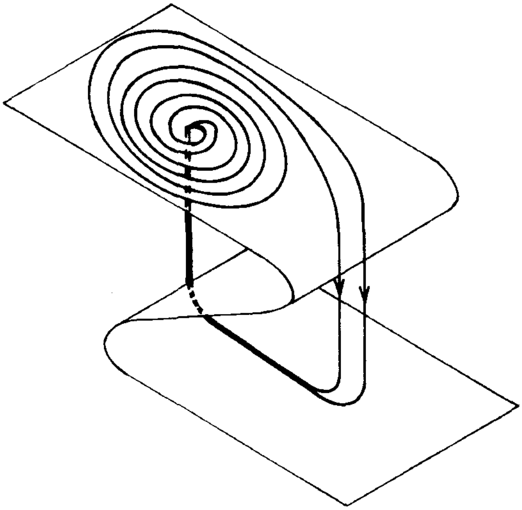

Figure 28. A qualitative picture of a chaotic flow that can be derived as a perturbation of the periodic trajectory of figure 26(*b*).

(1973) soon drew attention to chemistry, the first experimental evidence of chemical chaos only appeared in 1978–1979 (Rössler and Wegmann 1978, Hudson *et al.* 1979, Vidal *et al.* 1979, Sorenson 1979). Let us summarize how deterministic chaos exhibited by chemical systems: (i) looks like, (ii) is characterized by, and (iii) emerges from more familiar behaviours.

We have already mentioned complex oscillations where 'small' and 'large' amplitude variations appear to be mixed in a random way, without any periodicity at least on laboratory time scales (figure 5 (*a*)). How can we be confident that the 'dwarfed' oscillations reflect the chemical dynamics rather than an imperfect experimentation (as believed at first)?

A statistical argument is provided by the fact that several groups, working in different countries with different apparatus, have reported very similar observations. Moreover, dynamical regimes characterized by a noisy Fourier spectrum† (see figure 5 (*b*)) are obtained in the course of experiments which lead to perfectly periodic regimes (see figure 1 (*b*)) for the same set of experimental conditions except a nearby flow rate. It is striking to note that:

(1) when occurring, the sequences of alternating periodic and chaotic regimes are reproducible, with a regular trend in an increase of the 'noise' level from one chaotic regime to the next (Vidal *et al.* 1982),
(2) chaos is not always found, even when very complex periodic regimes are identified (Maselko and Swinney 1985),
(3) typical routes leading from periodicity to chaos have been observed in full qualitative agreement with the theoretical predictions made for low-dimensional dynamical systems (see below). Randomness cannot be a source of such well-defined sequences of events.

Another powerful method for studying dynamic regimes is to look at phase portraits. Ruelle and Takens (1971) made the breakthrough while introducing the concept of 'strange attractor' which is the core of our present understanding of chaos. Let us remind ourselves of the two main features of this highly non-intuitive mathematical object:

(1) it has a 'fractal' structure (and dimension) consisting of an infinite set of sheets, generated by an infinite sequence of stretching and folding operations,
(2) onto a strange attractor, trajectories starting from nearby points diverge exponentially fast (on the average), a property known as 'sensitive dependence on initial conditions'.

When dealing with experimental results, phase-space analysis must overcome a real difficulty. Only a single phase variable—say $X(t)$—is usually recorded. However, it has been conjectured that the topological properties of the attractor in the true (unknown) phase-space would be preserved in image spaces involving as independent coordinates:

either: $X(t),\ \dot{X}(t),\ \ddot{X}(t), \ldots$	(Packard *et al.* 1980)
or: $X(t),\ X(t+\tau),\ X(t+2\tau), \ldots$	τ being an arbitrary time delay (Takens 1981)

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† The Fourier spectrum (or the power spectrum) displays how the power density $P(f)$ (i.e. square root of the sum of the squares of the real and imaginary parts of the Fourier transform of a time series) depends on the frequency f.

Hence, it thus becomes possible to analyse phase portraits reconstructed from any single time series $X(t)$.

Figure 29 shows the result so obtained in a space $(X, \dot{X}, \ddot{X})$ with a non-periodic regime of the BZ reaction. At the bottom of the plot, the clockwise trajectories may either go directly upwards, or else, enter the eddy where they make an undefined number of turns before leaving. Therefore one cannot predict how the distance between two points will evolve. This is exactly what sensitive dependence on initial conditions means. Following a method invented by Poincaré at the turn of this century, it is efficient to look at the intersection of the attractor with a well chosen surface.† Depending upon the topological nature of the attractor—limit cycle, T^2 torus, strange attractor—one will get a Poincaré section consisting in a point, a closed curve, or a set of lines (one for each sheet) respectively. Figure 30 (*a*) presents a projection onto a plane $(B(t+\tau), B(t))$ of the attractor corresponding to another dynamical regime of the BZ reaction (Roux and Swinney 1981). The Poincaré section by a perpendicular plane (passing through the dashed line in figure 30 (*a*)) appears in figure 30 (*b*). It looks like a segment, slightly curved. There the fractal nature of the attractor remains completely invisible, the sheets being packed very close one to another thanks to a high rate of dissipation. Still, recording the coordinate x (along the segment of figure 30 (*b*)) of successive intersection points yields a discrete sequence $x(n)$ which is plotted as one-dimensional map $x(n+1) = f\{(x(n)\}$ in figure 30 (*c*). Clearly, this first return map points out the deterministic character of the dynamics. Indeed one gets a single-valued curve, so that the value of any $x(n)$ determines unambiguously that of $x(n+1)$. Furthermore, the curve displays an extremum, thus fulfilling the theoretical requirement of a non-invertible map associated to chaos. In contrast, a stochastic process would have led to a set of points spread more or less all over the plane, since no relationship is to be expected between two successive intersections occurring at random.

Chemical systems seem to be highly dissipative so that their dynamics should be largely understandable in terms of one-dimensional-map properties. Maps with a single extremum have been theoretically studied in great detail and a lot of predictions are available which, very often, do not depend on the exact shape of the mapping: in that case, the corresponding behaviour is said to be 'universal'. For instance, any 1D-map having a quadratic extremum will give rise to a 'period-doubling cascade' by varying a bifurcation parameter. Here, an initial periodic regime loses its stability through a sub-harmonic bifurcation, thereby generating another periodic regime with approximately twice the period. This phenomenon repeats again and again, the period being doubled at each step. On the parameter axis, the points at which sub-harmonic bifurcation takes place rapidly accumulate. The asymptotic rate of convergence is governed by a 'universal' number $\delta = 4{\cdot}66920\ldots$; finally, chaos sets in. Many such cascades have been reported over the past few years, including in chemistry. Because the control parameter used is the flow rate, only the first three period-doubling bifurcations have been observed with the BZ reaction (see figure 6; Simoyi *et al.* 1982).

Another nice prediction, which even applies to non-quadratic extrema, deals with the so-called U(niversal)-sequence. It states the order in which periodic windows appear along the bifurcation axis, beyond the first accumulation point. A periodic

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† In practice this method is applied in general to three-dimensional spaces, the surface often being merely a plane. Obvious reasons of convenience put these two restrictions at work in most cases, even though they are not at all required in principle.

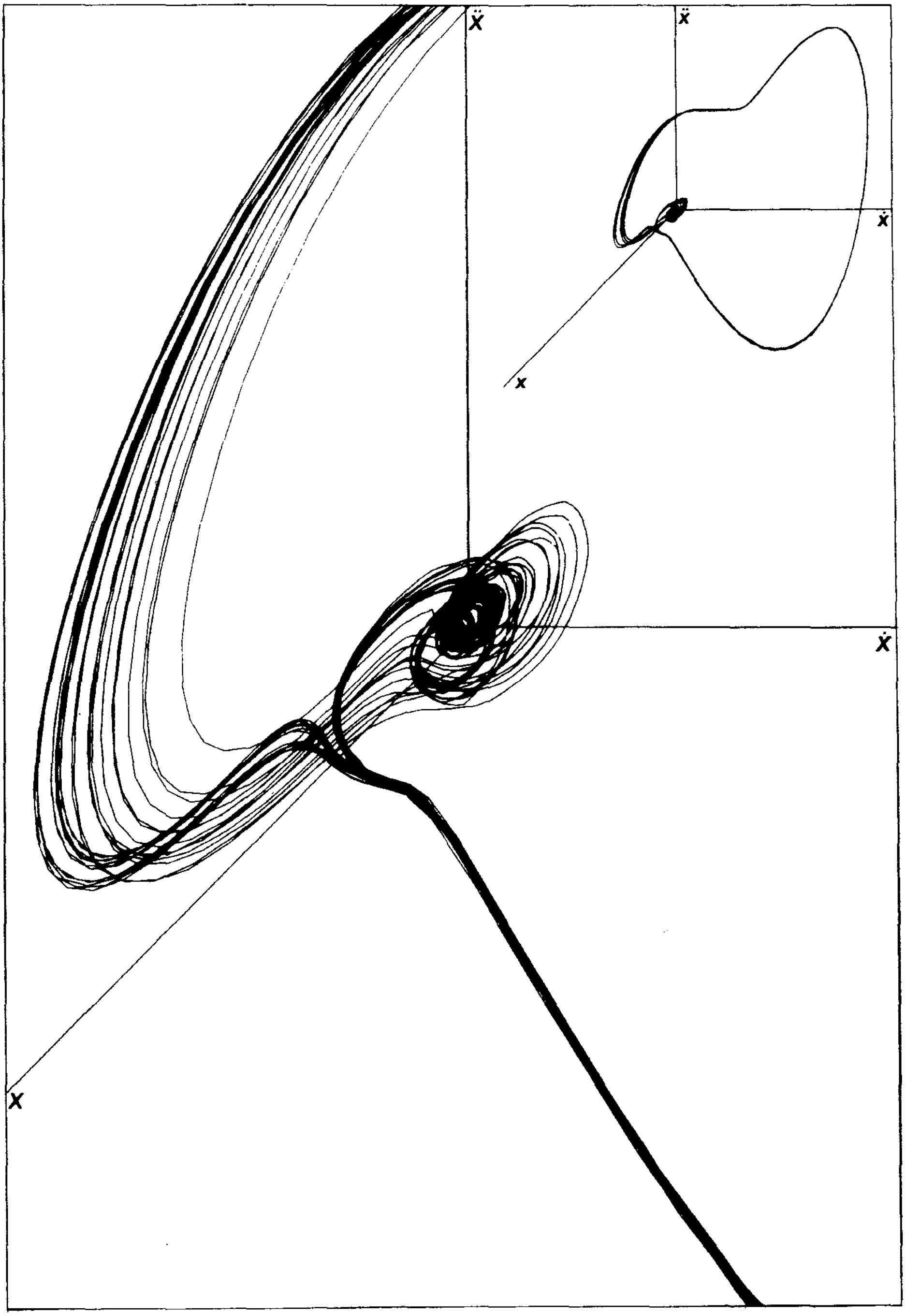

Figure 29. Phase-space portrait of a non-periodic regime of the BZ reaction (Roux *et al.* 1980). The whole attractor is represented in medallion, while the blow up shows the region where trajectories diverge.

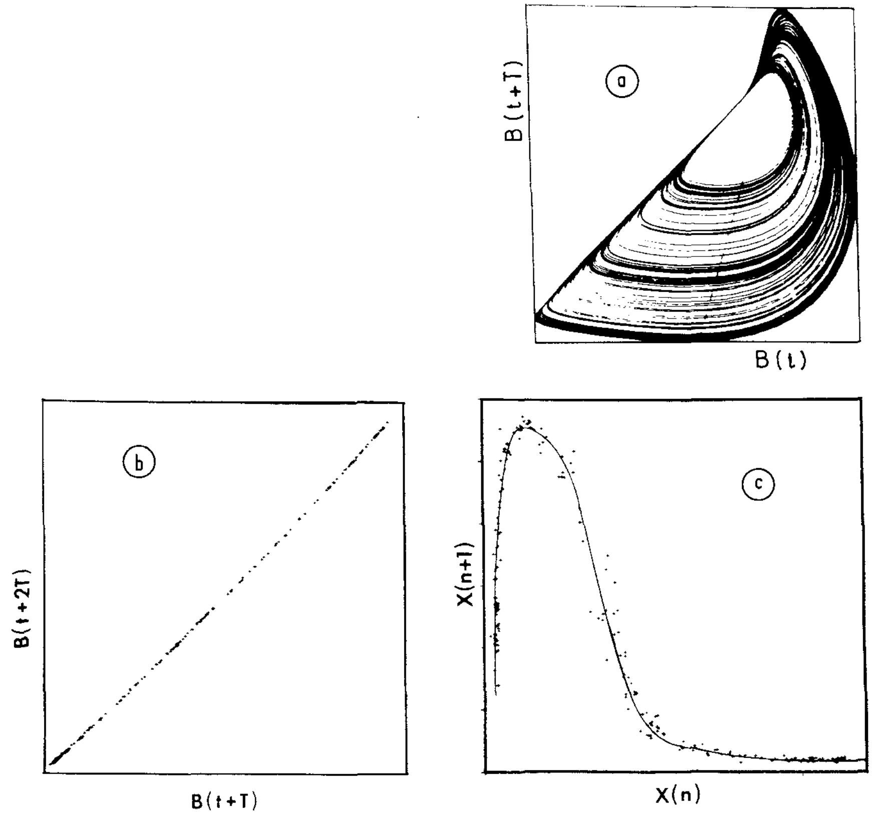

Figure 30. Phase-space analysis of a non-periodic regime of the BZ reaction (Roux and Swinney 1981). (*a*) 2D phase-space portrait. (*b*) Poincaré section of the three-dimensional attractor by a vertical plane passing through the dashed line in (*a*). (*c*) 1D-map constructed by plotting the successive coordinates x_n along the line obtained in (*b*).

window consists in a periodic P-cycle ($P > 1$), followed by its own period-doubling cascade. The perfectly-defined hierarchy of these P-windows forms the U-sequence (Metropolis *et al.* 1973). No discrepancy between the observed order of occurrence—sometimes, however, difficult to establish—and the prediction of the U-sequence was noticed (Simoyi *et al.* 1982).

Transition from periodicity to chaos may also occur via ‘intermittency’. This phenomenon was theoretically predicted by Pomeau and Manneville (1980), once again analysing the general properties of 1D-maps. Intermittency consists of rather long periods of nearly periodic oscillations, interrupted from time to time by bursts of ‘noise’. Three different types of bifurcation may generate such a behaviour. Type I intermittency results from a saddle–node bifurcation taking place when the mapping curve becomes tangent to the first bisectrix (see figure 31 (*a*)). Before this, the two intersection points stay apart. At tangency, these two points coalesce. Slightly beyond, a narrow channel is created between the first bisectrix and the mapping curve. The system spends a considerable amount of time in crossing this channel (see arrows) and develops nearly periodic oscillations during this whole period. When the iteration point leaves the map to the right and is then reinjected in the channel on the left, a burst

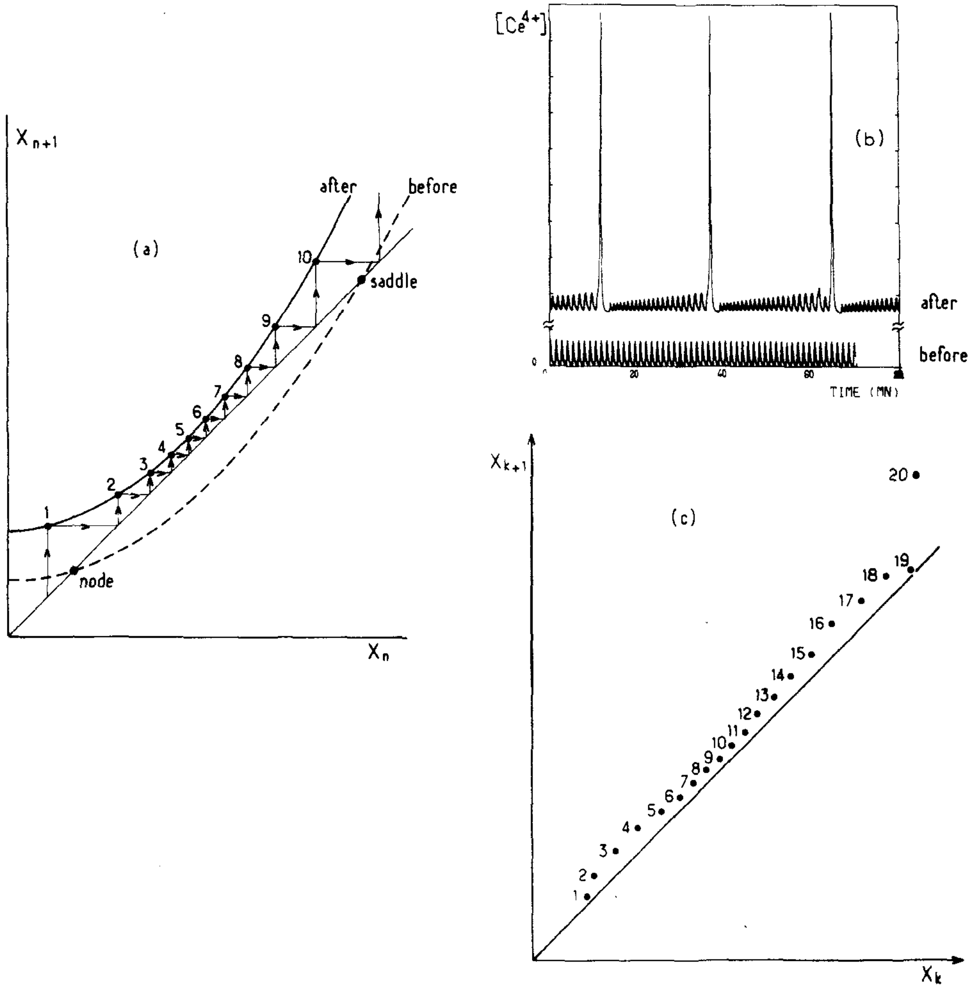

Figure 31. Type I intermittency (Pomeau *et al.* 1981). (*a*) Theoretical 1D-map (Pomeau and Manneville 1980). (*b*) Time series record of the BZ reaction. (*c*) Next amplitude plot deduced from (*b*) and very similar to (*a*).

of noise (not depicted by the map) occurs. In accordance with these theoretical predictions, figures 31 (*b*) and (*c*) display the experimental observations made on the BZ reaction by Pomeau *et al.* (1981). It is worth noting that the agreement between theory and experiment goes beyond the qualitative view obvious in figure 31.

Several other experimental data have been collected about the dynamics of the BZ system. However, these are less well understood and call for further research (Turner *et al.* 1981, Vidal and Rossi 1981, Vidal *et al.* 1982, Roux and Rossi 1984, Argoul and Roux 1985).

Needless to say, many computer simulations have already been carried out. Several attempts using oversimplified models seeking for chaos have failed (Showalter *et al.* 1978, Ganapathisubramanian and Noyes 1982, Schwartz 1984). Owing to the large number of experimental data which fit theoretical predictions so nicely, these shortcomings do not really cast doubt on this field. Indeed:

(i) given a model, the dimension of the parameter (rate constants, concentrations, etc.) space is such that exploring a significant part of it would require a huge number of simulations;

(ii) the BZ reaction has a very complex chemistry, as discussed before. Thus the relevance of any simplified model is always questionable;

(iii) a seven-variable model, derived from the Oregonator, does exist already which exhibits chaotic regimes. Moreover, it leads to phase portraits and 1D-maps resembling that of figure 30 (Ringland and Turner 1984) and provides an alternating periodic–chaotic sequence similar to experimental findings (Turner *et al.* 1981). No doubt this model is as relevant as any other one.

3.12. *Analogy with phase transitions*

At this point, it is worth noting the very fruitful analogy that can be drawn between bifurcations in dynamical systems and phase transitions.

Bistability has all the qualitative properties of first-order transitions. We shall see later that not only static but also dynamical properties find their equivalent. For instance, the transition from one state to the other can occur by a nucleation process, and there exists a critical point (see figure 18).

The Hopf bifurcation, on the other hand, provides an equivalent of a second-order transition (figure 22), in which the amplitude of the limit cycle is the order parameter, null before the transition, increasing after. We even find a classical exponent of one-half in that case.

Similarly, chaos presents various regularity and even universality properties, including scaling properties with universal exponents, and renormalization concepts have been fruitfully applied to characterize the structure of strange attractors.

One should not be too much surprised to find a rather close, at least qualitative or topological, analogy between processes of change, no matter how we call them: transitions, bifurcations or even catastrophes.

3.13. *General mathematical aspects*

The modelling of the dynamical behaviours that we have described previously relies entirely on classical chemical kinetics, in the sense that no new ingredient is required, except for the fact that the system is kept far from equilibrium by some external constraint, typically by a feed of reactants as in a CSTR. We are thus left with a set of differential equations derived from mass-action kinetics, in which the external or control parameters are the rate constants, the flow rate in a CSTR, and the concentrations of inputs:

$$\frac{dX_i}{dt} = \dot{X}_i = G_i(X, K), \quad i = 1, \ldots, N$$

where the X_i are the concentrations of the N internal species, and K denotes a vector of parameters. The first question is: how many steady states are there, and at what concentrations? The steady states X^s are simply defined by:

$$G_i(X^s, K) = 0, \quad \forall i$$

There is no general and practical answer to this question. Notice that at equilibrium this question does not arise since, due to the property of detailed balance, there is only one equilibrium state. We keep the term 'steady state' as the general one.

Considering one particular steady state, the second question that one has to face is: is this steady state stable?

Linear stability analysis can, in principle, give an adequate answer. This is achieved by examining the eigenvalues of the matrix:

$$A_{i,j}=\left.\frac{\partial \dot{X}_i}{\partial X_j}\right|_{X^s},\quad i,j=1,\ldots,N$$

where the derivatives are evaluated at steady state. In practical situations, this is not a simple task.

Finally, we shall have to analyse the behaviour of the system when instability occurs. This requires us to take into account non-linear terms, a very complex and tedious task for which no universal procedure is available. One usually ends up performing computer simulations, without being able to avoid many trial-and-error steps, due to the lack of any rational methodology to perform such a modelling project.

There is still a lot to be done in designing efficient and practical analytical and computer tools to help the chemist in his modelling effort. Nevertheless, we shall sketch some of the results that contribute to this project.

A number of studies, not only in the field of chemical kinetics, have tried to answer the question of linear stability: for instance, the theory of 'Qualitative Stability of Matrices' (Quirk and Ruppert 1965). Other works have taken into account the specific dynamical properties of chemical kinetics, namely mass-action law, that put a set of constraints on the general mathematical problem exposed above. For instance, all the diagonal terms of matrix A are non-positive as long as the reaction scheme involves only mono and bi-molecular steps (Hanusse 1972, 1973). This property rules out the existence of limit cycle oscillations around an unstable steady state in models with only two intermediate species. It is important to realize that most of the exotic behaviours that we are considering result from the interaction of a small number of variables. Mathematically we would say that they represent low-dimensional dynamical behaviours. Unfortunately, in real situations, we have to deal with many more variables, i.e. species, than we can practically handle. This is why the study of formal models (table 1) was so important to assess the chemical pertinence of such exotic mathematical objects.

Other interesting results have been obtained in trying to classify the types of instability that can result from chemical processes. It has been possible to show (Tyson 1975) that all destabilizing processes in chemical reaction networks can be classified as:

direct autocatalysis
indirect autocatalysis (positive feedback loop)
end-product inhibition (negative feedback loop)

As an example of these notions, let us consider the following reaction step:

$$\mathrm{A}+2\mathrm{X}\rightarrow 2\mathrm{X}$$

Obviously it belongs to the first class and, in term of mass balance, it could be written as:

$$\overset{\text{act.}}{\overset{\curvearrowleft}{\mathrm{A}\rightarrow\mathrm{X}\rightarrow\mathrm{B}}}$$

which indicates that X activates its own production. But in the same class, one also has steps like:

$$\mathrm{A}\rightarrow\mathrm{X}\overset{\overset{\text{inh.}}{\curvearrowright}}{\rightarrow}\mathrm{B}$$

where X inhibits its own degradation.

Of course such criteria will only tell us whether a particular reaction scheme is able to produce an amount of instability in its steady state. It will never tell for which values that can be achieved, if it is physically possible, and what behaviour will develop therefrom.

A global 'chemical network' type of approach has been used by several authors, leading, for instance, the 'Zero Deficiency Theorem' (Feinberg and Horn 1974), which defines a large class of chemical networks that cannot be unstable, under any circumstances. Similarly, Clarke (1980) has designed a 'Stoichiometric Network Analysis' which still appears as a complex approach to a chemist, but seems to be amenable to practical applications (Clarke 1984).

Finally, we must say a word about the development of still more effective practical methods, which can be used by 'ordinary' chemists, through a computer simulation system. They try to incorporate as much as possible of the mathematical tools, still being constructed, to allow a more rigorous and systematic analysis of the dynamical behaviours which can arise in conditions far from equilibrium. A first step in this direction is provided by computer simulation systems which present a chemist-friendly interface, making possible a quick, versatile and safe design and simulation of chemical models (Gottwald 1979, Hanusse and Richetti 1985). They can offer various specific tools, such as steady-state calculation and linear stability analysis, reaction step-rates monitoring, data-file management and display, etc. But, although they do help the chemist in his modelling task, they are essentially simulation tools rather than real Computer Aided Modelling Systems. There is still a need for what we could call an 'Expert System in Chemical Dynamics', through which the mathematical expertise in dynamical systems and bifurcation theory could be applied with more intelligence, and could be made available to the chemists in their own language. In this way might be achieved a more realistic modelling of experimental systems, the pertinence of which could rely on a rational methodology.

So far, we have dealt only with deterministic dynamics as derived from a description in terms of differential equations. We should mention here, without going into much detail, that stochastic dynamics has also been considered, mainly in theoretical works, although a few experimental investigations have been performed to study the role of fluctuations, internal or external, in particular near instability points. This stochasticity has nothing to do with chaos, although the term has sometimes been used by theoreticians. Chaos is a non-periodic deterministic behaviour. Here we refer to non-deterministic dynamics that result mainly from the molecular nature of chemical processes, whose microscopic dynamics are not described in detail but manifest themselves either through fluctuating control parameters—in that case one speaks of external fluctuations—or through a stochastic description, for instance in terms of birth and death processes (Gardiner 1983). In this case one speaks of internal fluctuations, and the set of differential equations is replaced by a Master Equation describing the evolution of the probability density $P(X,t)$ for having a composition X (particle numbers) at time t. External fluctuations are usually taken into account by adding a fluctuating force to the r.h.s. of the deterministic differential equations (that can also be done for internal fluctuations with an appropriate term) leading to a stochastic differential equation (Horsthemke and Lefever 1984).

It is particularly important to understand the role of fluctuations near instability points, where several possible paths of evolution are usually offered to the system. Besides, the analogy between bifurcations and phase transitions appear to be deeper when one realizes that fluctuations could behave in a rather universal way. Computer simulations have shown that, for instance in a bistable system, a nucleation process can be observed (Hanusse 1977, Hanusse and Blanché 1981 a, b, Boissonade 1982), and that some kind of critical behaviour can be observed near the triple point (Hanusse 1981).

Unfortunately very little has been done experimentally in this field. No way has been found to observe directly fluctuations, and experiments on external noise are rare and rather dubious. It may be that the study of spatial structures will provide a grip, although indirect, on some aspects of the role of fluctuations in dissipative chemical systems.

4. Spatial and spatio-temporal behaviours

4.1. *Introduction*

Since the experiment performed by Bénard at the turn of this century, convection has been well known as a source of spatial organization in fluids. One expects, however, according to an analysis first developed by Turing (1952), some chemical reactions to be able to give rise to spatial ordering. The highly non-linear character of their kinetics makes chemical oscillators good candidates for providing direct experimental evidence. As a matter of fact, many patterns have been observed in BZ and BZ-like media for more than fifteen years. At the beginning several of them were poorly understood, while a few were clearly misinterpreted. To prevent errors, it seems appropriate to set up a classification, even though the vocabulary has not yet reached its final stage in this domain.

Until now, two different types of spatial behaviour have been experimentally identified:

(i) reaction–convection patterns (to which presumably belong the so-called 'mosaic structures'),
(ii) reaction–diffusion phenomena known as chemical waves ('trigger waves' or 'auto-waves').

On the one hand, it must be emphasized that the oscillatory character of a chemical reaction is not a requirement for the appearance of such behaviour in a reacting medium. Several examples will be given in this paper. On the other hand, it should be realized that spreading an oscillating medium onto a surface may give rise to other time–space dependent phenomena. Nonetheless, the corresponding 'waves' are of a very peculiar kind. Originating from a spatial desynchronization (in phase or frequency) of the oscillation, their 'propagation' does not involve diffusion. Thus they have properties drastically different from those of ordinary (i.e. diffusion-dependent) waves. We find it convenient to make hereafter a clear distinction, by calling them 'pseudo-waves'.

Before going into more detail let us add that yet another type of 'wave' was theoretically predicted by Ortoleva and Ross (1973) and by Hagan (1981). However, we will not discuss this further, because no experimental observation has been reported so far.

Though spatial structures and waves have been observed in 1D(imensional), 2D (Pétri dish), or 3D (tube) devices, most results come from experiments performed on shallow layers. Accordingly, attention is mainly paid to this case in the remainder of the paper. Let us simply recall that three-dimensional scroll waves raise both fascinating topological questions (Winfree and Strogatz 1983) and serious experimental problems (see plate 5; Welsh *et al.* 1983).

4.2. *Reaction–convection patterns*

Structures of this type may occur in a reacting medium, whether oscillatory or not. Typical examples are provided by experiments involving a monotonic reaction taking place at an interface. Most often, the medium is kept out of equilibrium by continuous light irradiation (Möckel 1977, Kagan *et al.* 1982, Gimenez and Micheau 1983, Avnir *et al.* 1983) which, moreover, initiates a photochemical reaction (plate 1). Sometimes, also, the liquid layer is merely put into contact with a suitable vapour (Avnir and Kagan 1983). In all these cases, the reaction is monotonic and never exhibits an oscillatory character. When a light beam is used, depending on the (ir)reversible nature of the photochemical process, the structure either disappears (photochromic compound) or remains (chromogenic compound) when the light is switched off.

The most striking property of these structures is that they are 'unmoving' patterns: they grow, exist and, eventually, vanish 'at the same place' (at least on usual experimental time scales). This fact illustrates a clear difference from the waves, whose front propagates regularly through the layer at a speed of several millimetres per minute.

Qualitative studies of such stationary patterns have been carried out on photochemical systems. There are many systems of this kind. A few were discovered by Möckel (1977), and many others four years later. Chemical compositions appear in Avnir *et al.* (1983), and Gimenez and Micheau (1983). The way in which a pattern emerges in the layer has definitely been elucidated in several (but not all) cases by Micheau *et al.* (1983). Using the schlieren photographic technique, these authors have shown that convection occurs and leads to what they call 'pre-patterns', even if a reaction does not take place. More precisely, a slow convection motion is induced by a Rayleigh–Bénard instability, an adverse density gradient being produced by evaporative cooling of the solvent. If the photochemical reaction then sets in, it simply reveals to the eye these pre-existing convection patterns, the organic dye being trapped in regions having a downward velocity field. It is likely that some structures observed by Avnir *et al.* (1983) can be interpreted in a very similar way. Indeed, in this problem one has to take into account two different types of instability, each of them having two possible origins:

(i) the Rayleigh–Bénard instability, induced by an adverse density gradient resulting from evaporative cooling of the solvent and/or an endothermic reaction at the interface,

(ii) the Marangoni instability, inhomogeneities in surface tension arising from differences in temperature and/or chemical composition.

Therefore, one can expect an extremely complicated interplay between all these phenomena. This provides us with a rather simple qualitative explanation of the large variety of forms which have been observed in various reacting media. However, we are thus faced with a serious experimental challenge: namely, to set apart the different contributions whose relative importance certainly changes from one case to the other.

It is worth noting that certain observations reported by Avnir and Kagan (1984) seem to proceed through another type of mechanism. By 'sandwiching' between two plates a solution, of ferricyanide for instance, evaporative cooling and Marangoni-type effects are prevented. Nevertheless structures of Turnbull's blue are still formed by illuminating the layer. According to these authors the photoreduction starts over the entire surface at the upper part of the layer, prior to the onset of convection, but the mechanism by which the structure is formed remains so far mysterious.

Oscillatory as well as excitable BZ or BZ-like media are also known to yield very similar unmoving patterns, as reported by Zhabotinsky and Zaikin (1973), Showalter (1980) and Orbán (1980). Named for a while 'mosaic structures', they too are suspected to be reaction–convection patterns. The present guess is that, due to a reaction with oxygen in the air, inhomogeneities in chemical composition develop at the surface of the liquid. In this way a Marangoni effect triggers convection which is supplied, later on, by Archimedes' force. Two qualitative facts support this point of view:

(i) mosaic structures develop only in layers sufficiently deep (say 1·5 mm or more),
(ii) they are unobserved when the upper surface is not free, but put into contact with a plate.

Direct experimental characterization of convection motions is still lacking, once more, to convert this assumption into a firmly established result. Furthermore, recent calculations performed on the Oregonator show that they might be reaction–diffusion patterns as well (Becker and Field 1985).

4.3. *Pseudo-waves*

As we noticed before, a pseudo-wave[†] originates from spreading a time-periodic reaction whose oscillation phase and/or period is space-dependent. This will produce an apparent propagation throughout the reacting medium whereas nothing actually moves. In other words, pseudo-waves are basically an optical illusion: the chemical analogue of those electric signs whose lights are successively switched on and off. Their velocity is inversely proportional to the gradient producing them and, thus, becomes infinite when this gradient vanishes. The main characteristic of such waves is that diffusion is not involved at all in their 'propagation'. Accordingly, 'pure' pseudo-waves can never be observed in a continuous medium because diffusion sets in as soon as concentration gradients appear. However, provided the time scales of diffusion and apparent propagation are sufficiently different, so that diffusion remains always negligible,[‡] the concept of pseudo-waves is really useful in understanding the two following salient features:

(1) a high propagation velocity (with respect to that of diffusion) having no upper limit,
(2) the crossing of impermeable barriers, because diffusion plays no role in the phase propagation.

[†] Here, we will adopt a single term—pseudo-wave—whereas at the beginning a distinction was made between kinematic waves (Kopell and Howard 1973 a) associated to a period (or frequency) gradient and pseudo-waves (Winfree 1972) due to a phase gradient. This distinction is rather academic and it seems more appropriate to use only two 'flags', one for reaction–diffusion phenomena ('true' waves) and a second for diffusion-free propagation, whatever the nature (phase and/or frequency) of the gradient.

[‡] The same kind of approximation is made for reaction–convection patterns: diffusion and convection time scales are assumed to be such that no significant coupling takes place.

These pseudo-waves provide us with nice pictures or films (see plate 4 section 2.2.2; Sadoun-Goupil *et al.* 1982), but they have very little—if any—scientific interest. We mention them only to emphasize that propagation-like phenomena, which are not diffusion-dependent, may occur in an oscillating medium. These should not be mistaken for chemical waves, as they were sometimes at the very beginning of research in this area (Busse 1969).

4.4. *Chemical waves*

'Chemical wave' must be hereafter understood as having the following very precise meaning: a propagation phenomenon due to coupling between diffusion and chemical reaction, and nothing else. There is nowadays general agreement that certain structures exhibited by either an oscillating reaction, an excitable medium, or even a bistable one, belong to this category. Experimental as well as theoretical arguments support this point of view:

(i) no experimental evidence that convection, heat transport, or surface tension play a significant role, at any stage, is known;

(ii) analytical calculations and computer simulations based on the classical reaction–diffusion equation:

$$\frac{\partial X}{\partial t} = F(X) + D\Delta X \tag{2}$$

X	concentration vector
$F(X)$	reaction term
$D\Delta X$	diffusion term according to Fick's law
D	diffusion coefficient matrix

although carried out on simple models yield results which agree qualitatively and, sometimes, semi-quantitatively, with experimental data.

As mentioned above, many data come from 2D-experiments performed with the BZ reaction. Expanding rings of chemical activity spontaneously develop in BZ reagent thin layers at rest. They propagate outwards, starting from a point named 'centre', and form a pattern which looks like a target (plate 3). These target patterns are easily seen in visible light, using the redox ferroin/ferriin catalyst. Commonly, the medium stays in the red reduced state (Fe^{2+}), whereas a ring is a blue zone of oxidation (Fe^{3+}). At low malonic acid concentrations, the opposite (red-on-blue) pattern can be observed (Smoes 1980).

Breaking a circular wavefront developing in an excitable medium may give rise to a pair of rotating waves (Winfree 1972, Zhabotinsky and Zaikin 1973): the two free ends created wind up in opposite directions (clockwise and counter-clockwise), forming a pair of spirals. A more elaborate recipe (Agladze and Krinsky 1982) enables one to produce multi-armed rather than single-armed spirals (Plate 2). However, it must be emphasized that spirals do not emerge in a quiescent layer until a previously existing wavefront has been perturbed.

Circular waves, leading to disc and target patterns, also appear spontaneously in chlorite–iodine–malonic acid solutions (De Kepper *et al.* 1982). Though not really surprising, this experimental fact demonstrates the need for a general interpretation of this behaviour, which must not depend too much on the detailed chemical mechanism.

Excitable and bistable media are well fitted for initiating single waves, for instance by applying a suitable voltage between two electrodes. Once triggered, the wave propagates autonomously. One thus gets either a front in a bistable system (there is a switch from one state ahead of the front, to the other behind it), or a pulse in an excitable one (ahead and behind the pulse, the system is—almost—in the same state). Both types have been thoroughly investigated in the case of the iodate–arsenious acid reaction† (Hanna *et al.* 1982, Rastogi *et al.* 1983).

The propagation mechanism of all these chemical waves can be qualitatively depicted in the framework of a reaction–diffusion process as follows. A wavefront is a narrow area where steep concentration gradients of several species exist. It is the diffusion of certain species across their own gradient which triggers the reaction ahead of the front. Accordingly, when two opposite wavefronts collide, they must annihilate one another,‡ as must the corresponding gradients. As a matter of fact, one observes that such an annihilation does always occur as expected (see examples in plate 3). Furthermore, assuming the triggering species to be ions, one predicts that propagation will be sensitive to an external electric field applied in the direction of wave motion. Recent experimental data confirm this point of view. A negative electric field (i.e. whose direction is opposite to that of wave propagation) accelerates the waves up to five times for $E = 40\,\mathrm{V\,cm^{-1}}$; whereas a positive field slows them. For positive electric fields higher than $10\,\mathrm{V\,cm^{-1}}$ a splitting of the wave is even induced, thereby initiating new wave(s) moving in the reverse direction (Sevcikova and Marek 1983).

If we now look to more quantitative features, it is noteworthy that rather few data are available, except on wave velocities. These and their dependence on concentrations and temperature in BZ media are gathered in table 4. The analysis of wave profiles had been undertaken only very recently (Wood and Ross 1985). No experimental measurement to, at least, figure concentration gradient(s) in a wavefront has been

Table 4. Wave velocity dependence on (*a*) concentrations and (*b*) temperature for the BZ reaction measured in thin layers (except † tubular reactor).

(*a*) *T* (K)	W.V. $= a + b[\mathrm{H_2SO_4}]^{1/2}\,[\mathrm{BrO_3^-}]^{1/2}$ *a* ($\mathrm{mm\,min^{-1}}$)	*b* ($\mathrm{mm\,min^{-1}\,M^{-1}}$)	References
298	−0·832	27·87	Field and Noyes (1974 a)
298	−1·957	25·86	Showalter (1981)
291	−3·2	28·3	Wood and Ross (1985)
298	−0·83	27·9	Kuhnert *et al.* (1985)
298	−3·43†	58·34†	Sevcikova and Marek (1983)

(*b*) Range (K)	W.V. $= f(T)$ ($\mathrm{mm\,min^{-1}}$)	
285–298	$5 \times 10^6 \exp(-4100/T)$	Wood and Ross (1985)
284–318	$9 \times 10^6 \exp(-4200/T)$	Kuhnert *et al.* (1985)
288–303	$-58{\cdot}55 + 0{\cdot}21\,T$†	Sevcikova and Marek (1983)

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† Here the front converts the solution of initial reactants to the equilibrium composition.

‡ *Therefore a pulse travelling in an excitable medium has nothing to do with a soliton*, even though no dispersion is detected (Wood and Ross 1985).

reported until now. The lack of such significant information points out how far the experimental study of chemical waves still remains incomplete. Finally, Müller *et al.* (1985) have shown very recently that the diameter of the core of a single-armed spiral (i.e. the central zone where the variations of ferroin concentration are tenfold lower than outside) does not exceed 30 μm.

4.5. *Modelling problems*

The coupling between chemical and hydrodynamic processes raises very difficult theoretical problems. Extensive studies are carried out in the gas phase, because combustion and flame propagation have such great importance. Comparatively, much less consideration is paid to what happens in liquids. Anyway, no attempt has been made so far to reach a quantitative description of the stationary reaction–convection patterns recalled in section 4.2. Pseudo-waves do not deserve any special analysis, since they are formally the $D \rightarrow 0$ limit of a wave. Therefore, the question readily reduces to that of chemical waves.

Still, the challenge remains to account for single waves, wave trains and rotating waves propagating either in bistable, excitable or oscillating media. Beyond the general form of equation (2), both the chemistry and the boundary conditions may be chosen at will, of course. As a natural consequence, many different models have been studied analytically and/or numerically, under many different conditions. They have in common a limited number of free species (three at most) and a diagonal diffusion coefficient matrix (which sometimes reduces to a single term). For a survey and comments, the reader is referred to Fife (B 1979) and Vidal and Pacault (R 1982). In short, whatever the medium's characteristics, there is finally no major problem to design a model and to select conditions such that a wave, a target pattern, a spiral (Archimedean or logarithmic) will eventually result. More interesting is the fact that certain models enable us to get the proof that these solutions are stable and, thus, quite observable. Postponing to the next section the general mathematical background, let us present here two models which bring a deeper insight to the physical nature of target patterns.

The first relies on a fully determinstic approach, designed by Tyson and Fife (1980) to meet the conditions encountered in the 'Z' reagent (Winfree 1972); that is, excitability. Worthy of mention is the fact that this model provides results in good agreement with experimental data—in particular wave velocities—on both rings (Tyson and Manoranjan 1984) and spirals (Fife 1984). The basic ingredients are:

(i) a set of two dimensionless differential equations, derived from the Oregonator suitably reduced and scaled, whose variables X and Z are respectively proportional to $HBrO_2$ and Fe^{3+} (ferriin). Only the diffusion of $HBrO_2$ is considered for the sake of simplicity; and

(ii) the existence, at the centre of a target, of an heterogeneity, i.e. a 'catalytic' particle (dust, scratch, etc.) which locally modifies the kinetics.

As seen in figure 32, which displays the null clines in the phase plane (Z, X), the system is in a stable steady state (point A), but excitable: a small deviation from A to the right will drive the system along the large excursion BCDA. Moreover, the catalytic particle is assumed to shift the kinetics slightly in such a way that, right at the centre, the steady state is no longer stable and the reaction oscillates. Thus the centre periodically induces a perturbation in its neighbourhood, by locally increasing $HBrO_2$ concentration. A wavefront of $HBrO_2$ autocatalytic production is triggered (line AB in

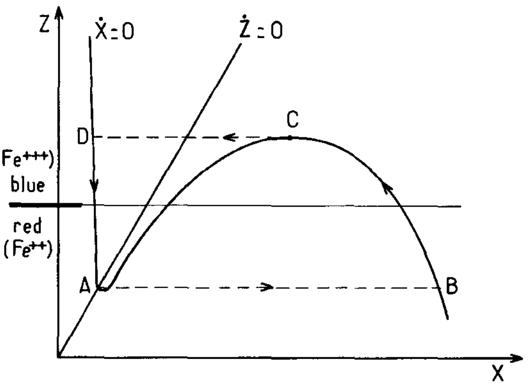

Figure 32. Phase-plane portrait of Tyson's modelling of waves in excitable BZ media (Tyson and Manoranjan 1984).

figure 32). Between B and C the colour of the dye switches from red to blue. Then there is a wave of $HBrO_2$ destruction (line CD) corresponding to the back front of the pulse. The system slowly goes back from D to A, while the red colour is restored. In the medium, each oscillation of the centre gives birth to a blue annulus of oxidation which propagates outwardly in a red medium. Thanks to a suitable modification of the constants, one can easily explain in a similar way the red-on-blue patterns observed at low malonic acid concentration. This time, of course, the first wavefront corresponds to $HBrO_2$ destruction, whereas the pulse ends by $HBrO_2$ production. Beyond this qualitative picture, the model predicts values of wave velocities in fairly good agreement with the experimental findings. This, in turn, gives additional support to the Oregonator itself.

On the one hand, wave propagation in an excitable medium is finely described by this model but, on the other, the hypothesis about catalytic particles can hardly be falsified. Now there are several other models showing that heterogeneity is not at all necessary to account for target patterns. Furthermore it seems experimentally established that 'homogeneous' centres could exist, at least in oscillating media (Zaikin and Kawczynski 1977). Walgraef *et al.* (1983) have proposed an alternative explanation of wave emission in two-dimensional oscillating systems which does not involve any extra singularity. Their approach relies on a stochastic analysis of the problem, taking into account phase fluctuations of the chemical oscillation. According to their theoretical calculations it turns out that, beyond an instability threshold, a fluctuation is able to create a centre from which waves are radiated periodically. The main point is that a centre is now a direct product of oscillations and, consequently, target patterns and oscillatory behaviour are no longer independent: several relationships exist between their properties. Using the Brusselator (table 1) and assuming local fluctuations to be 'Gaussian white noise' distributed, Walgraef *et al.* (1983) have derived some of them. Figure 33 shows, for instance, how the fraction of centres is expected to depend on the wave number of emitted waves, and how the number of centres should vary with the amplitude of oscillation.

In the framework of this stochastic approach, and whatever the model, statistical correlations must be observed as soon as centres result from a fluctuation–nucleation mechanism. On the contrary, heterogeneities would give rise, in principle, to complete

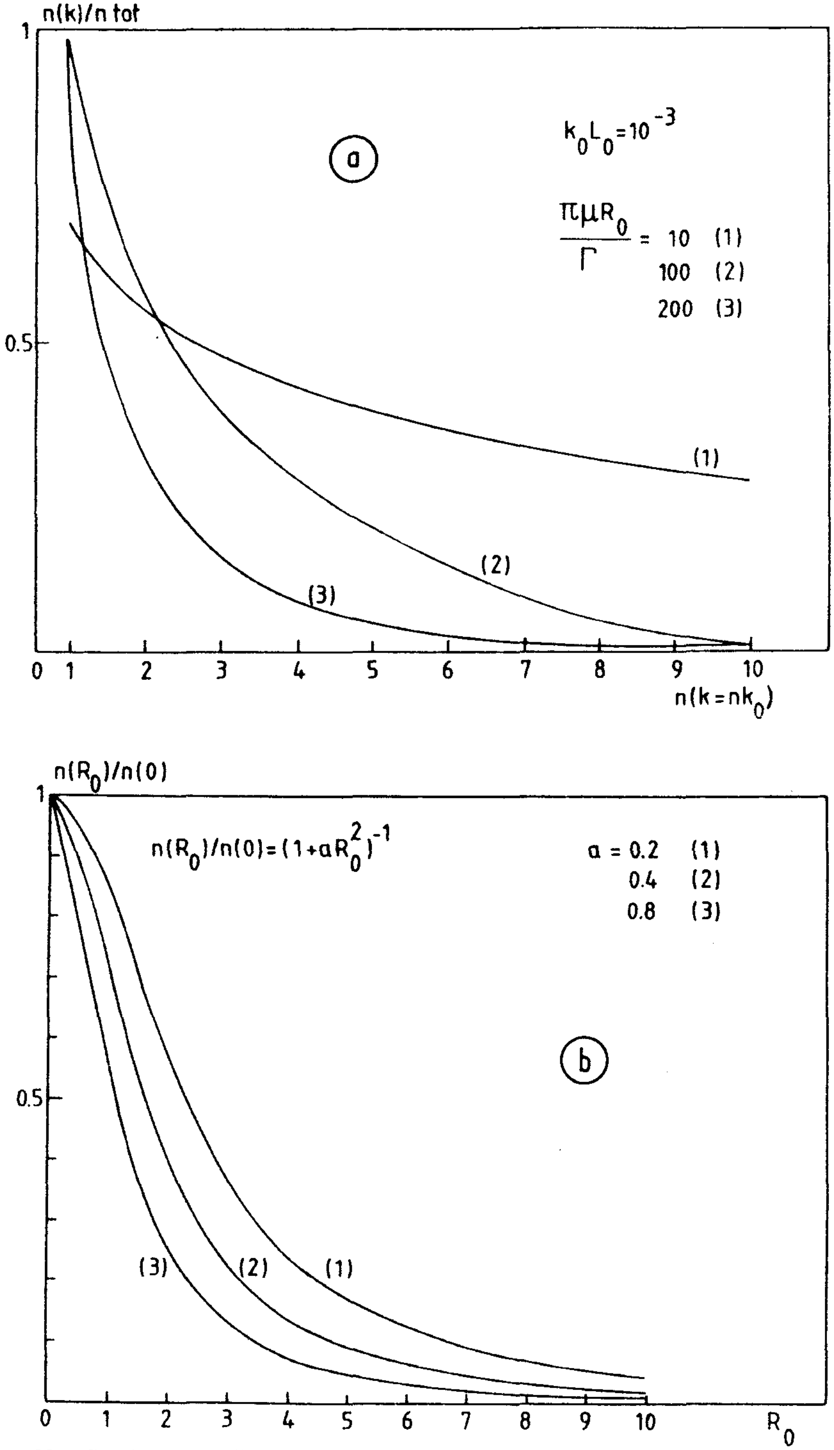

Figure 33. Stochastic predictions about target patterns in two-dimensional oscillating systems (Walgraef *et al.* 1983). (*a*) Fraction of centres versus wave-number. (*b*) Total number of centres versus the limit cycle amplitude R_0.

randomness. Reliable experimental observations of statistical properties have not been realized so far. The task is yet a real challenge. Of course, many data have to be collected to get a statistically significant sample. But the essential problem to be overcome is to lower as much as possible the influence of (otherwise unobservable) external sources of centres: 'catalytic' particles and fluctuations are not mutually exclusive.

4.6. *General mathematical aspects*

Though the experimental tools available at the present time only permit observation of transient evolutions, the theoretical question which is addressed is that of asymptotic solutions of equation (2). More specifically, we are interested in the existence and stability of these solutions. However, because (2) is a partial differential equation,† little can be done and there is no general answer to these two questions. One can only recognize different types of solution, which may exist, especially the familiar example already encountered:

(i) space-independent time-periodic solutions (i.e. homogeneous oscillations),
(ii) space-dependent time-independent (i.e. stationary) solutions,
(iii) travelling waves (pulses, wave fronts, wave trains),
(iv) rotating waves (spirals, scrolls).‡

The initial and boundary conditions play a great role, as also does the Euclidian dimension of the system. In this context, one easily understands how difficult it is to carry out detailed studies without specifying particular conditions, especially about the reaction kinetics. As a consequence, one is quite naturally led to perform numerical simulations, despite the lack of generality of a study devoted to a particular model. Among many others, let us mention the Brusselator (Herschkowitz–Kaufman 1975) and the Oregonator (Reusser and Field 1979, Becker and Field 1985) which, in one-dimensional space, exhibit stationary structures and waves. In two spatial dimensions, expanding rings and spirals have been numerically obtained with several different models (e.g. Gul'ko and Petrov 1972, Kuramoto and Yamada 1975, 1976), while the Brusselator yields rotating waves too (Erneux and Herschkowitz-Kaufman 1977). Apart from such 'classical' reaction–diffusion simulations, the cellular automaton designed by Greenberg and Hastings (1978) also deserves to be noticed although it does not rely on equation (2): this two-dimensional 'game of life' produces spirals and circular waves.

Whatever their own interest, all these computer simulations leave unanswered the question of the general conditions required to get a solution of a given type and to make it stable. One can hope to learn something about this from analytical calculations, provided they are not devoted to very particular cases. Passing over many studies dealing with specific models, we shall rather focus our attention on more general approaches yet available. To get, say, 'universal' results, one must obviously reduce as far as possible the set of preliminary hypotheses. In particular, the chemical mechanism should remain largely unspecified. This is the reason why it is necessary to assign to the reaction terms $F(X)$ nothing more than a 'qualitative' feature (e.g. time-periodic, near a Hopf bifurcation, excitable, etc.) without going into further details.

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† Of course, equation (1) is derived from equation (2) by eliminating all spatial derivatives. Accordingly asymptotic solutions of the 'kinetic' set (1) are also (space-independent) solutions of (2). However their stability with respect to inhomogeneous perturbations is no longer ensured.

‡ According to Winfree (1973) a scroll is a spiral projected in three dimensions either by translation, or by revolution around a distant axis, thereby forming a 'scroll ring'.

In this framework, various theoretical analyses have been reported to account for target patterns and spirals developing in a two-dimensional medium of infinite extent. Dealing with target patterns a crucial assumption is that of an heterogeneity at the centre. In a 'smoothly' oscillating (i.e. not relaxational) medium, Ortoleva and Ross (1973) were the first to predict the existence of 'phase waves' leading to target patterns whose size expands proportionally to the square root of time. More recently Hagan (1981) has derived a similar, but more rigorous analysis.† In both cases a third term is added to equation (2) to describe the influence of a local heterogeneity. However, as we have already recalled, a singularity is not at all a prerequisite: homogeneous-centre theories are available as well (Bose *et al.* 1980, Kopell and Howard 1981). Worthy of mention is a particular form of equation (2), suggested by Kopell and Howard (1973 b), the so-called λ–ω systems:

$$\frac{\partial X}{\partial t}=\begin{pmatrix}\lambda & -\omega\\ \omega & \lambda\end{pmatrix}X+\Delta X$$

$$X=\begin{pmatrix}X_1\\ X_2\end{pmatrix}\quad \text{time-periodic function (limit cycle)}$$

This fairly general two-variable equation, although restricted to oscillatory media, enables us to derive a rigorous proof of several results. Thus, circular waves are actually stable solutions of it. Various rotating spirals also exist for certain λ–ω systems, but their stability is not yet firmly established (Greenberg 1980, 1981). Enlarging such an approach to an n-variable system undergoing a Hopf bifurcation, Hagan (1982) has shown that one-armed spiral waves are probably stable, whereas multi-armed ones are unstable.

Finally, Winfree and Strogatz (1983) have recently undertaken a geometrical analysis of scroll waves in excitable media. Using only topological arguments, they seek for the limited set of spatial arrangements compatible with a reaction–diffusion process. Situations as complicated as twisted and/or knotted scroll rings, even mutually-linked by pair, are investigated. This is the first and very qualitative attempt to explore the problem of three-dimensional wave anatomy, at least in this chemical context.

The Master Equation approach mentioned earlier has been used to study some reaction–diffusion systems in the presence of fluctuations. A number of qualitative effects have been detected in one-dimensional systems, such as the bimodal probability distribution in a bistable system and the associated nucleation process due to the coupling with diffusion, or the effect of Hopf bifurcations, which may change from supercritical to subcritical due to the mean field effect of local fluctuations (Hanusse 1977).

Stochastic analysis of reaction–diffusion processes in two-dimensional space is still at its beginning. In the previous section we recalled the theory of target patterns developed by Walgraef *et al.* (1983). In the same paper, the probability of vortex-like phase fluctuations—which would result in rotating spirals—is shown to be vanishingly small. Therefore, spirals are not expected to form spontaneously and, unless initiated, should not be observed. This is as yet the only available analytical result. Numerical simulations involving Monte Carlo methods are also rather few. Specific algorithms

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† An experimental observation of target patterns exhibiting the predicted properties is still lacking, presumably because chemical oscillations are mostly of relaxation type.

have been designed to improve these computer-time consuming approaches. The two-dimensional $X3$ Schlögl model (table 1) has been investigated as an example of non-equilibrium phase transition leading to critical behaviour (Hanusse 1981). A similar nucleation process has also been observed using a molecular dynamics technique (Boissonade 1982). These few studies have remained essentially qualitative, mainly because no analytical treatment could be carried far enough to define some guidelines, direction of search, or specific assumption to be checked quantitatively; secondly because no experimental access to these phenomena has been discovered. It may well be that the experimental investigation of the random aspects of spatial structures will give some handle to the effect of fluctuations near bifurcation points.

5. Conclusion

After fifteen years of steady developments, the achievements of the large variety of studies on non-equilibrium chemical dynamics and related fields can be measured and appreciated as a remarkable contribution to the universality of knowledge.

Looking from a distance, we could summarize up the concerns of these studies by the word 'morphogenesis', i.e. creation of shape and structure from the uniform and homogeneous. One might point out that others have tackled this very problem even more explicitly, biologists as well as mathematicians. In fact, morphogenesis, in the broadest sense, is probably one of the central paradigms of the last decades. It is of course no surprise that such a convergence of interests has occurred, which simply confirms its universality. But, as it turns out, chemistry appeared to be at a good level, between the complex reality of living systems and the reducing abstractions of mathematical descriptions, to allow a direct investigation of the universality of behaviours itself.

Shapes are change and rhythm, evolution and structure. We have seen the analogy between the changes in phase transitions and those in bifurcations. The analogy works for deterministic as well as for stochastic aspects. Fluctuations, as a source of evolution which does not exclude determinism, appear to play an important role, although localized at some 'turning points'. On the contrary, we have learned that determinism does not necessarily imply predictibility, as in chaos. Here, from the complete knowledge of a trajectory, nothing can be inferred, as we are used to do, concerning the future of a close, no matter how close, but distinct trajectory.

One realizes that the experimental modelling of such complex systems and behaviours, yet simple as compared to the structure and evolution of living systems, remains an extremely difficult task. We can no longer satisfy ourselves by using oversimplified abstract models, usually based on pure intuition; neither can we carry out experiments without bearing in mind what we have learned of the universal behaviour of evolving systems. Unfortunately, there is still a lack of tools to connect the universal descriptions and their observed implementations in experimental systems; not only practical tools, but also intellectual ones, to characterize the universal in the particular, and to reduce the particular to the universal.

This is already difficult to achieve for many simple temporal behaviours, as soon as one pretends to describe most of their qualitative features. It is necessarily much more difficult for spatial behaviours. Considering that most of what could be obtained by simple means, in modelling experimental temporal homogeneous behaviours, has been reached, clearly the understanding and control, of spatial behaviours, of unpredictibility, both stochastic and chaotic, of heterogeneous aspects, remain as outstanding challenges. It should be considered as an example of the present-day attempts, in many fields of science, to design new and specific tools to investigate the complexity of nature.

Appendix

A BZ reagent exhibiting oscillations and chemical waves

Readers who have never seen the behaviours we are dealing with are strongly encouraged to experiment with the BZ reaction. It is so easy to handle and so nice to look at! Standard chemicals are readily available and no special care is required. Contamination by Cl^- ions, which poison the BZ reaction, must be thoroughly prevented; beware that certain commercial ferroin solutions do not fulfil properly this condition. At room temperature, the following aqueous reagent gives rise to oscillations in a stirred vessel, and to target patterns (Plate 3) when poured onto a surface so as to form a layer of approximately 1 mm depth:

BrO_3Na : 0·30 M
H_2SO_4 : 0·010 M
$CH_2(COOH)_2$: 0·08 M
Ferroin : 0·004 M

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