

Major unsolved problems await the adventurous. The rate constant expressions 7 and 9 should be refined to include explicit solvent effects. The concept of phonon-induced vacancies⁵⁵ may have to be incorporated into a rate theory addressed to the liquid state. The normalization of the overcomplete basis sets⁹ in the intersecting harmonic approximation for the DM configuration requires further consideration. The QSM rate theory has been applied to electron-transfer reactions

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in condensed media^{56,57} and surface diffusion phenomena.⁵⁸ Further generalization to chemical reactions is mostly an exercise in the proper choice of R and an appropriate perturbation to promote the transition between the equilibrium reactant and product configurations.

Parting from the transition-state theory of rate processes in condensed media has opened up a research field that is still virtually untouched. Hopefully this Account will serve to focus attention on the future of this exciting new field.

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Phenomena in Homogeneous Chemical Systems Far from Equilibrium

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During the course of a chemical reaction the concentration of the chemical species either passes through a single extremum or else attains monotonically a steady-state concentration. This statement is still widely believed by chemists, except for some chemical engineers more familiar with instabilities occurring in continuous chemical reactors.^{1,2} Indeed, in some critical conditions these reactors may exhibit striking oscillations in temperature and composition due to the heat of reaction; in these systems rate constants are very sensitive to temperature, and these reactions may be involved in a feedback loop. Such instabilities are known as thermokinetic phenomena and are treated in chemical engineering texts. They are not the subject of our present attention.

Other known physicochemical oscillations, such as Liesegang rings, periodic crystallizations, periodic dissolution of metals in acid, catalytic decomposition of hydrogen peroxide by mercury, periodic adsorption of

gas, enzymatic reactions in colloidal solutions, and electrochemical oscillations, take place in heterogeneous medium.³⁻⁶

Oscillations in homogeneous media were long considered impossible, although there seems to have been some early experimental evidence of homogeneous oscillating reactions. The reaction of hydrogen peroxide and potassium iodate in dilute aqueous sulfuric acid solution observed by Caulkins and Bray in 1917 and published in 1921 by Bray⁷ is the first experimental evidence of oscillating behavior in an homogeneous chemical reaction, if one suspects, as Bray does, the periodic evolution of carbon monoxide during the dehydration of formic acid in sulfuric acid described by Morgan⁸ in 1916 to be heterogeneous. More recently, Belousov⁹ (1959) reported sustained oscillations in the oxidation of citric acid by potassium bromate catalyzed by ceric sulfate in dilute aqueous sulfuric acid. This reaction and its variants were extensively investigated

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by Zhabotinskii¹⁰ in the early 1960's. To our knowledge it is the only reaction that exhibits both temporal and spatial structures. In addition there are many periodic biochemical reactions, such as the horseradish peroxidase catalyzed aerobic oxidation of NADH found by Yamazaki et al.,¹¹ or the anaerobic glycolytic pathway, on which a great number of papers have been published.¹²

As will be mentioned below, thermodynamics shows that sustained oscillations in a chemical reaction may only arise in a system open to matter or energy exchanges with its surroundings.¹³ Two good reviews of the thermodynamic theory of chemical oscillations have been published.^{13,14}

We want to make scientists more aware of the unusual phenomena encountered in homogeneous chemical systems held by constraints far from thermodynamical equilibrium. Because of the unusual features of the chemical reactions treated in this Account, it is necessary to introduce a suitable definition of the terms employed (see Table I). First we shall talk about experimental features of these chemical instabilities in homogeneous reactions, and then account for their kinetic interpretations. The latter are based on hypothetical reaction schemes, mainly chosen for their mathematical tractability. Although generally non-realistic, they give qualitative explanation of the causes of the observed phenomena and may also give the clue for still unexpected observations.

Experiments

In order to illustrate temporal and spatial behavior in real chemical reactions evolving far from equilibrium, we shall describe recent investigations in this domain.

Temporal Organizations. Reliable experiments on sustained oscillations in homogeneous chemical reactions should fulfill the theoretical conditions mentioned above and summarized in the second part of this paper. These theoretical conditions could easily be provided by a continuous-flow stirred-tank reactor. Actually there have been quite a few experiments performed in a continuous-flow reactor, but there is an increasing interest in experiments driven in these conditions.

We have investigated the $\text{H}_2\text{O}_2\text{-KIO}_3\text{-CH}_2(\text{COO-H})_2\text{-MnSO}_4\text{-HClO}_4$ oscillating reaction¹⁵ (which resembles the oscillating reaction of Bray, but operates at room temperature with greater amplitude in oscillations) in a very convenient type of continuous-flow stirred tank reactor.^{16,17} It is the most complete study of an homogeneous oscillating reaction performed under these conditions which exhibits all the interesting phenomena observed separately in other reactions, such

Table I
Definition of Terms

Constraints	Variables that might be controlled by the experimenter (for example concentrations or flows)
Surroundings or external medium	The whole set of constraints
Responses	Variables measurable by the experimenter; all the responses are very rarely measured.
System	The whole set of responses
Object of investigation	Conjunction of the system and its surrounding
State of the object	A set of values of the responses for a given set of constraints

as: sustained oscillations,¹⁸ multiple stationary states,^{17,19,20} excitation,^{21,22} and composite oscillations.^{19,23,24} In these experiments, the constraints are stirring, light intensity, temperature, pressure, residence time τ (ratio of the total flow rate to the reactor volume), and the concentrations $[A_i]_0$ of the inlet species A_i after mixing and before any reaction. The responses (Table I) measured are the temperature, the oxidation-reduction potential E , and the absorption of light due to iodine, an intermediate species produced during the chemical reaction.²⁵

State Characteristics. Qualitatively one may distinguish sustained oscillating states from steady nonoscillating states. Sustained oscillating states have very stable frequency, with a relative accuracy usually within 5×10^{-3} . The fast addition of an amount of intermediate species in the reactor disturbs the oscillations, but they recover their initial form after a while. This stability to perturbations is characteristic of a limit cycle behavior.²⁷ Oscillation can last forever, as long as reactants are provided. Indeed, one has an illustration of a real thermodynamical clock beside atomic clocks and astronomical clocks.²⁸

State Diagram. Depending on the values of the constraints, sustained oscillations or steady states are observed in the reactor; it is then possible to establish, in the constraints space, the critical surface separating these two classes of states.

Figure 1 shows an example of sections in the $([2\text{CH}_2(\text{COOH})_2]_0, [\text{KIO}_3]_0)$ plane of the state diagram. Periods of oscillating states are largely dependent on the values of the constraints; they are given in seconds in

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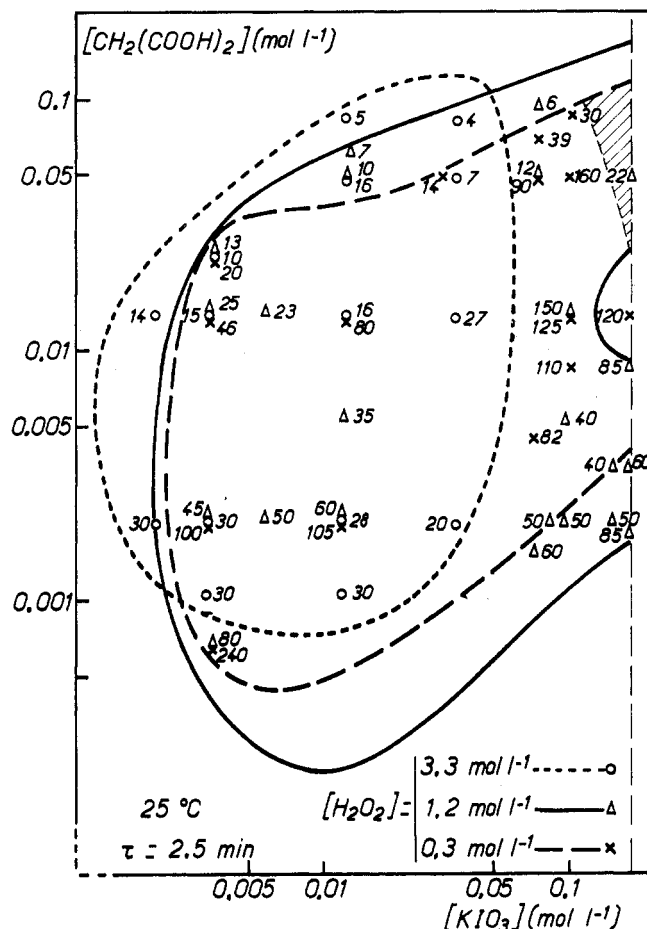


Figure 1. Sections in the $([CH_2(COOH)_2]_0, [KIO_3]_0)$ plane of the state diagram. The numbers give the periods in seconds.

Figure 1. A great number of sections of the state diagram are available in ref 17. Depending on the region of the constraint space, the transitions from one class of states to the other by change of constraints exhibit very different characteristics. The transition may either show smooth changes in the amplitude of the limit cycle which fades at the transition point or, in contrast, present a jump in the average value of the responses. In this last case the limit cycle disappears with a finite amplitude. Sometimes for the same set of constraints there may exist several states, steady state or oscillating. This happens in the shaded regions of Figure 1, where a sustained oscillatory state coexists with a steady state, the system being on either of them depending on the initial conditions of the experiment. In these regions, transitions may also occur for a fixed set of constraints, by a perturbation: i.e., the fast addition by the experimenter of a small amount of an intermediate chemical species in the reactor.

Multiple Stationary States. Let us suppose the system to be in an oscillating state, B (Figure 2). The experimenter decreases constraint C on a time scale larger than the relaxation time of the system. For a critical value, C_s , of the constraint, the system regime changes abruptly to a nonoscillating state, inducing a steep variation of the average value in the iodine concentration. Now, if we reverse the evolution of the constraint C , the system remains in this steady state until the constraint reaches another critical value C_0 ($C_0 \neq C_s$) where oscillatory process is recovered with a

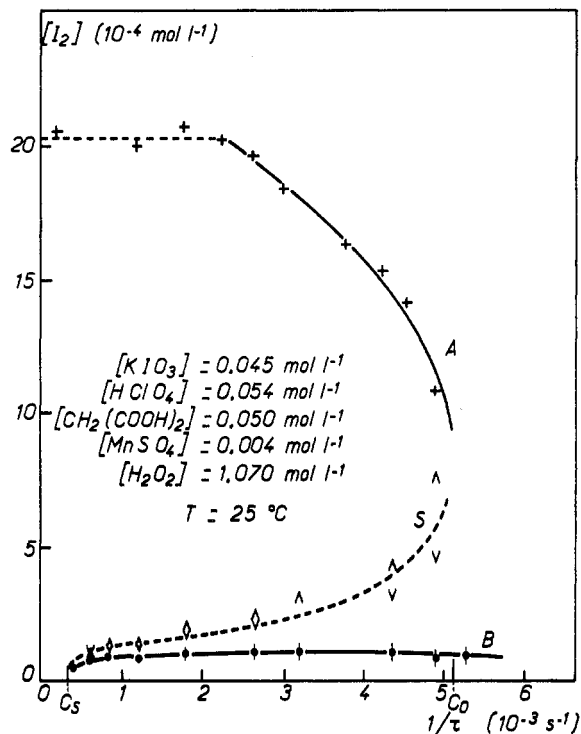


Figure 2. Multiple stationary states (constraint:residence time).

discontinuity in iodine average concentration. If one decreases again constraint C , the system will remain in an oscillating state until $C = C_s$.

The spontaneous transition between oscillating and steady states only happens for two characteristic values C_0 and C_s of the constraint. Then, for any value of the constraint between C_0 and C_s , the system may be on either state A or state B: it is a bistable system. Transition from one state to the other is not "invertible"²⁹ since there is a hysteresis phenomenon. Now, for a given value of the constraint between C_0 and C_s , one can trigger transitions from one state to the other by a perturbation. This has been done by producing a steep variation in the iodine concentration in the reactor. If after this perturbation the system, temporarily drawn from its stationary state, goes back to its initial state, the perturbation is said to be regressive and quoted "V"; if, for a greater perturbation, the system shifts to the other stationary state, the perturbation is said to be nonregressive and quoted "A" (Figure 2). Between these two cases, for different values of the constraint, a threshold line of perturbation (dashed line) points out the frontier between regressive and nonregressive perturbations.

Figure 2 illustrates the evolution of a bistable system as a function of the inverted ratio of the residence time τ (this quantity is proportional to the total flow rate through the reactor). Here $C_0 = 1/\tau_0 = 5.1 \times 10^{-3} \text{ s}^{-1}$ and $C_s = 0.3 \times 10^{-3} \text{ s}^{-1}$. Stationary steady state corresponds to high concentration in iodine (curve A). It is interrupted for values of iodine concentration greater than $20 \times 10^{-4} \text{ mol l}^{-1}$, the value above which solid iodine appears in the mixture. Curve B corresponds to the second state; as a function of the constraint $C = 1/\tau$ this state shows sustained oscillations (vertical segments

(29) We distinguish, with Duhem, the "invertible" feature of a chemical reaction (as they are represented by $\sum \nu_i A_i = \sum \nu'_i A'_i$) from a "reversible" process in which a chemical reaction may be involved. Indeed, chemical reactions proceed very often far from thermodynamical reversibility.

Table II
Reaction Schemes

I	1920, A. J. Lotka $A = B$	$A + X \rightarrow 2X$ $X + Y \rightarrow 2Y$ $Y \rightarrow B$	First theoretical model to predict sustained chemical oscillations, but oscillations are marginally stable.
II	1952, A. M. Turing $A + 2B = D + E$	$A \rightarrow X$ $X + Y \rightleftharpoons C$ $C \rightarrow D$ $B + C \rightarrow W$ $W \rightarrow Y + C$ $Y \rightarrow E$ $Y + V \rightarrow V'$ $V' \rightarrow E + V$	Spatial structure
III	1968, I. Prigogine and R. Lefever $A + B = D + E$	$A \rightarrow X$ $2X + Y \rightarrow 3X$ $B + X \rightarrow Y + D$ $X \rightarrow E$	Limit cycle; chemical waves; localized and nonlocalized spatial structures
IV	1970, B. Edelstein $C = B$	$C + X \rightleftharpoons 2X$ $X + Y \rightleftharpoons Z$ $Z \rightleftharpoons Y + B$	Multiple steady states; hysteresis
V	1972, C. Vidal $A + 2B = D + E$	$A \rightleftharpoons Y$ $B + Y \rightleftharpoons X + Y$ $2X \rightleftharpoons D + X$ $Y + X \rightleftharpoons E$	Multiple steady states that can generate spatial organization
VI	1974, R. M. Noyes and R. J. Field $fA + 2B = fP + Q$	$A + Y \rightarrow X$ $X + Y \rightarrow P$ $B + X \rightarrow 2X + Z$ $2X \rightarrow Q$ $Z \rightarrow fY$	Limit cycle; excitability; was suggested by the mechanism of the Belousov-Zhabotinskii reaction
VII	1974, P. Hanusse $2A = B$	$A \rightarrow X$ $2X \rightarrow 2Y$ $Y + Z \rightarrow 2Z$ $X + Z \rightarrow B$	Limit cycle; spatial structures and spatiotemporal structures.
VIII	1975, J. Boissonade $A + 2B + 3C + D = P + P' + X'$	$A \rightarrow X$ $B + X \rightarrow 2X$ $D + X \rightarrow P$ $X \rightarrow X'$ $B + X' \rightarrow Y$ $Y \rightarrow Z + X'$ $C \rightarrow \alpha$ $2\alpha \rightarrow 2\beta$ $\beta + Z \rightarrow 2Z$ $\alpha + Z \rightarrow P'$	Composite double oscillations in flow reactor conditions.

indicate their amplitude) until the value of $C = 1/\tau = 1.1 \times 10^{-3} \text{ s}^{-1}$, below which it gives place to a damped oscillatory state.²² Between these two branches the threshold line S gives the minimum perturbation in the iodine concentration which triggers transitions from B to A states. This threshold line is not necessarily the locus of unstable states predicted by theory.

It is possible to have an opposite triggered transition by extracting iodine from the solution, dropping in the reactor a few milliliters of benzene, which rapidly floats on the reagent surface and is removed by an overflow pipe with a certain amount of iodine; if enough iodine is extracted, the oscillatory state is restored.

Composite Double Oscillation. Another striking behavior of this system is the composite double oscillation such as those observed in Figure 3 where for a given set of constraints there is a periodical burst and disappearance of higher frequency oscillations.

This can be understood as a periodic transition between two pseudostationary states, one of them having an intrinsic oscillatory character. A group of interme-

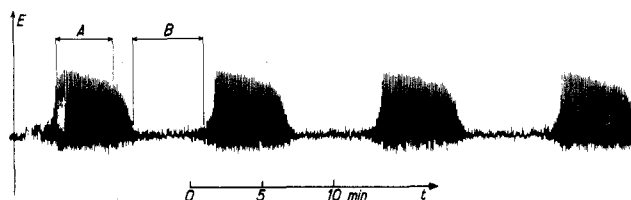


Figure 3. Composite double oscillation.

diating species of the system evolving on a larger time scale than the remaining one can then be considered as pseudoconstraints for the latter intermediate species; drifts of these pseudoconstraints are such that they flip-flop the system from one pseudostationary state to the other. A reaction scheme explaining this behavior has recently been developed (VIII, Table II).

Excitability. Let us have a stationary steady state; for perturbation (in $[I_2]$, for example) under a threshold value, the system relaxes rapidly to its initial steady state (a, in Figure 4). Perturbation over a threshold will induce a decrease in the iodine concentration, having

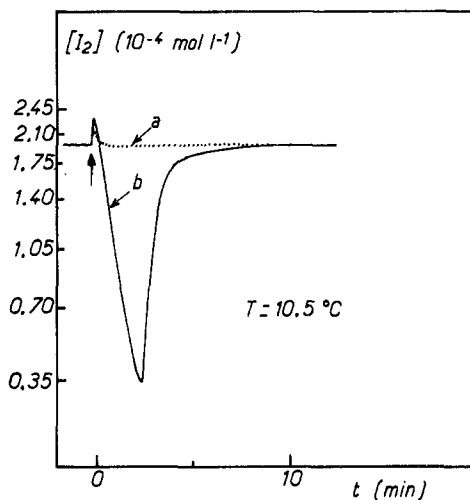


Figure 4. Excitability: (a) $[I_2]$ perturbation = $0.08 \times 10^{-4} \text{ mol l}^{-1}$; (b) $[I_2]$ perturbation = $0.10 \times 10^{-4} \text{ mol l}^{-1}$. Inlet concentration $[H_2O_2]_0 = 0.033 \text{ mol l}^{-1}$, $[KIO_3]_0 = 0.047 \text{ mol l}^{-1}$, $[CH_2(COOH)_2]_0 = 5 \times 10^{-3} \text{ mol l}^{-1}$; residence time, τ , = 2.6 min.

no correlation with the intensity of the perturbation; then, after a while, the system gets back to its initial steady state (b, in Figure 4).

If the response trajectories for perturbations under and over the threshold are very different, beyond this threshold the response trajectory is nearly independent of the intensity of the perturbation. This phenomenon of chemical amplification of a perturbation is known as excitability. It is often observed in the neighborhood of a sustained oscillatory state, and the response trajectory after excitation is very similar to that exhibited by the neighboring limit cycle.

Spatial Organization. The most striking example of spatial organization in homogeneous chemical systems is given by the reaction of Belousov-Zhabotinskii. Experiments are performed in a closed motionless reacting mixture, poured in thin tubes³⁰⁻³² or spread in thin layer in a dish.³³⁻³⁵ Although there is no energy or matter flux through the medium, structures may be observed because concentrations remain far enough from equilibrium values in the period following the initial mixture of chemical reagents. Thus spatial organizations stand with a more or less rapid drift in their characteristics and then disappear. However, no observed spatial structure is stationary, which is a situation quite different from what is known in the field of transport phenomena where Bénard³⁶ discovered stationary spatial patterns at the beginning of the century. In chemical systems only spatiotemporal structures known as chemical waves have been actually reported. These observations encompass two main wave phenomena, whether or not they depend on diffusion. The following description is mainly based on the very nice reports made by Winfree.³⁴

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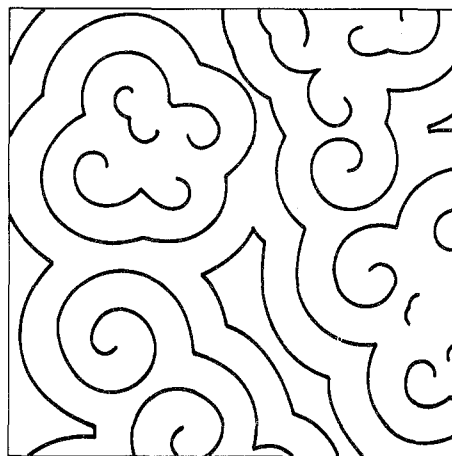


Figure 5. Spiral patterns of chemical waves in thin layer of reagent Z. The dark line represents the front head of the blue reduced region propagating through the reddish orange oxidized region. Each wave moves perpendicularly to its front.

Waves not depending on diffusion may be observed in any unstirred oscillating reaction. They result as not quite synchronous oscillations of the kind observed in the stirred solutions. This may be due to phase shifts in the bulk oscillations, temperature, or frequency-controlling compounds gradients. They are called *phase waves* or *kinematic waves*. Their velocity is inversely proportional to the steepness of the phase gradients and, so, has no upper bound.

Waves depending on diffusion: when Winfree's Z reagent, in which ferroin is both the catalyst and the redox indicator, is spread in a thin layer (about 2 mm) in a Petri dish, structures appear as travelling concentric vivid blue (oxidized) waves that emerge periodically from pacemaker centers, thus forming concentric rings like a bull's eye target pattern in a reddish orange (reduced) liquid. These waves are triggered at a heterogeneity (dust, scratch on the dish, bubble of CO_2) or by local fluctuations in the concentration; they are called *triggered waves* by Winfree. Their velocity is characteristic of the reagent (about 6 mm min^{-1} at 25°C). These waves mutual annihilate in head-on collision, and do not interfere like linear waves. Thus faster pacemakers (shorter wavelength) control domains which expand at the expense of slower ones. They are impeded by impermeable barriers introduced in the medium and are not reflected at boundaries. The circular patterns are unstable with respect to inhomogeneous perturbations, such as rocking the dish gently, and wind up into spirals as illustrated by Figure 5. In this geometry, chemical waves are self-renewing. That means that no pacemaker is required once they appear, and their wavelength is the smallest available in the reagent mixture. Winfree reported explanation of highly complex shapes of traveling bands, based upon the existence of a rotating three-dimensional scroll band of oxidation in the reagent. Unlike the first kind of waves, these latter are conducted through the medium and are based on its excitability properties and on dramatic diffusion conditions of chemical species.

Some Theoretical Aspects of Chemical Dissipative Structures

How might the phenomena described above be explained? Do they result only from particularly strange

reaction mechanisms? Do they satisfy some general conditions? Two levels are involved in the understanding of these phenomena: general thermodynamical theory and kinetic theory.

The thermodynamic theory has been extensively developed by the Brussels school.¹³ It is concerned with a large class of systems, chemical systems being only part of them. Certain general conditions are derived from this theory. The most important is that evolution must take place far from equilibrium. This means that external constraints must act on the system to prevent it from attaining the equilibrium state. These constraints may consist of fixing the concentration of some chemical species, or of fixing an inlet flow to it, as is achieved in a continuous-flow reactor. Then the system can only attain a stationary state. A most important result is that this stationary state may become unstable with respect to fluctuations and drive the system in a completely new situation where temporal or spatial organization may appear. These phenomena were called *dissipative structures* by Prigogine because they appear and are maintained thanks to a flow of energy or matter from the surroundings. From the thermodynamic theory, it follows that an instability of the stationary state can only occur if nonlinear kinetic processes take place in the system. Kinetic theory of chemical systems must be used to demonstrate formally the possibility of chemical dissipative structures. Starting with a reaction scheme one derives deterministic kinetic equations. By studying these kinetic equations several general conditions have been determined, such as the necessity of autocatalytic or cross-catalytic effects,^{13,37} or the necessity of at least three intermediate species when only mono- and bimolecular steps are involved in the reaction scheme.^{38,42} The method used in these studies can be presented briefly as follows.

The reaction scheme involved in the kinetic theory is a set of elementary reaction steps by which chemical constraints (A, B, C . . .) react by means of intermediate species or responses (X, Y, Z . . .). Concentrations of chemicals are assumed to obey classical kinetic laws, with an order equal to molecularity (van't Hoff law). Thus, for each reaction scheme, a set of first order, and generally nonlinear, differential equations may be written. If the scheme involves only mono- and bimolecular steps and if one takes into account diffusion according to Fick's law, these equations take the following form:

$$\dot{X}_i = \frac{dX_i}{dt} = R_i(X_j) + D_i \frac{\partial^2 X_i}{\partial r^2}$$

$$1 \leq i \leq n$$

X_i = concentration of i th intermediate species, D_i = the diffusion coefficient, r = space coordinate in a one-dimensional system, with

$$R_i = \mathcal{A}_i + \sum_j \mathcal{B}_{ij} X_j + \sum_j \sum_k \mathcal{C}_{ijk} X_j X_k$$

The first term, R_i , is the reaction term, the second one results from diffusion. \mathcal{A}_i , \mathcal{B}_{ij} , \mathcal{C}_{ijk} depend on rate constants and constraint values.

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Stationary states are obtained from $\dot{X}_i = 0$; $1 \leq i \leq n$. Once these states are known, it is important to determine their stability. This is achieved using the normal modes method:²⁷ kinetic equations are linearized around the stationary state in order to express the solution of differential equations around the stationary state as a linear function of exponentials:

$$X(t) = X_{st} + \sum_k a_k \exp\left(\omega_k t + i \frac{r}{\lambda}\right)$$

Here X_{st} denotes the stationary-state concentration, and λ the wavelength of the perturbation. For each value of λ the normal modes ω_k may be computed. If one of them has a positive real part the stationary state is unstable, since the corresponding exponential will increase in time. Therefore, depending on the value of kinetic parameters, the stationary state may be unstable with respect to homogeneous perturbations, that is for λ infinite, or to inhomogeneous perturbations, for λ lying in a finite domain, $\lambda_1 - \lambda_2$. In the first case, when there exist two unstable normal modes, a limit cycle type oscillation may eventually be observed. A limit cycle is an asymptotic cyclic trajectory in the space of intermediate species concentrations. The position and amplitude of the cycle are independent of their initial concentrations; thus the same sustained oscillation is recovered even after a perturbation in the concentration of intermediate species.

In the second case, only inhomogeneous perturbations are amplified, so that concentration gradients or periodic concentration profiles appear spontaneously from an initially homogeneous system. Fixed or propagating spatial structures may result from such an instability. The analytical investigation of dissipative structures near transition points, i.e. critical points where instability appears, has been developed recently by bifurcation theory,³⁹ and several theorems are available to investigate the stability of stationary state in purely chemical systems. These investigations have led to the analysis of reaction schemes which are not to be considered as reaction mechanisms of any existent reaction. Their study makes explicit the thermodynamic and kinetic conditions of occurrence of dissipative structures as well as their formation mechanism. *Computer experiments*, achieved with these reaction schemes by numerical methods or Monte-Carlo simulation, have permitted a significant advance in the investigation of deterministic properties of chemical dissipative systems. Stochastic properties were studied by numerical resolution of master equations,⁴⁰ molecular dynamics,⁴¹ and the Monte-Carlo method.⁴² This last method was used to provide direct evidence of the effects of local fluctuations such as stabilization of unstable stationary state or transition between multiple stationary states by nucleation processes predicted by stochastic theory.⁴³⁻⁴⁵ In this respect one finds that

(39) (a) G. Nicolis, *SIAM-AMS Proc.*, **8** (1974); (b) J. F. G. Auchmuty and G. Nicolis, *Bull. Math. Biol.*, **37**, 323-365 (1975); (c) M. Herschkowitz-Kaufman, *Bull. Math. Biol.*, in press; (d) J. F. G. Auchmuty and G. Nicolis, preprint.

(40) J. S. Turner, *Bull. Math. Biol.*, **36**, 205 (1974).

(41) J. Portnow, *Phys. Lett. A*, **51**, 370 (1975).

(42) P. Hanusse, (a) Thèse Docteur-Ingénieur, Université de Bordeaux-I, 1973; (b) Thèse d'Etat, Université de Bordeaux-I, 1976.

(43) I. Prigogine, G. Nicolis, R. Herman, and T. Lam, *Coop. Phenom.*, **2**, 1 (1974).

(44) M. Malek-Mansour and G. Nicolis, *J. Stat. Phys.*, **13**, 197 (1975).

(45) A. Nitzan, P. Ortoleva, and J. Ross, *Faraday Symp. Chem. Soc.*, No. **9**, 241 (1974).

phase-transition-like phenomena may occur in purely chemical dissipative systems.⁴⁶ Most of the phenomena observed experimentally during the last years have been predicted by the study of such reaction schemes.

Table II presents examples of reaction schemes studied by several authors. Lotka's model (I)⁴⁷ is the first example of a kinetic system exhibiting an oscillating behavior. These are conservative oscillations, not asymptotically stable as limit cycle ones. Turing's model (II),⁴⁸ the first proposed for spatial morphogenesis, leads to fixed spatial structures. Model III, often referred to as the "Brusselator",⁴⁹ has been widely studied by Prigogine et al. by analytical and numerical methods. It presents limit cycle oscillations as those described under Experiments, as well as fixed or oscillating spatial structures. It is the simplest reaction scheme giving rise to all these phenomena. Model VII^{42,50} presents the same phenomena without involving a trimolecular step as the Brusselator does. It was studied by the Monte-Carlo method. The mechanism of formation of a fixed spatial structure, as shown in Figure 6, was reported, and an oscillating structure of "vibrating string" type was observed.

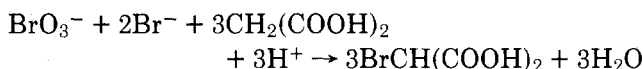
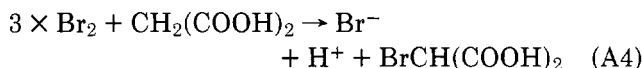
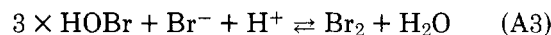
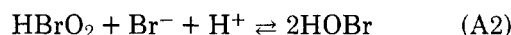
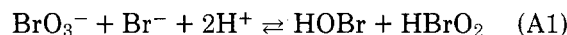
The existence of several stationary states for the same value of constraints is another interesting feature of dissipative chemical systems. Model IV⁵¹ is a very simple example of bistability. When the stationary-state concentration of some response is plotted as a function of constraint C , one obtains a typical Z-shape curve as in Figure 2. Given the value of C it may exist in two stable stationary states (lower and upper branch). A hysteresis phenomenon is then observed when the constraint is changed, transitions between the two states occurring for two values of the constraint, depending on the direction in which the constraint is moved. These features have been observed experimentally as reported in the first section. Excitability, also described previously, is related to bistability as well as nonperiodic spatial structures as those observed in V,⁵² Table II, or composite oscillations formally described by VIII.⁵³ Bistability was also studied in the frame of stochastic theory. Indeed, when concentration fluctuations are taken into account, transition from one state to the other no longer occurs for the values of constraint predicted by deterministic kinetic equations. The behavior of homogeneous fluctuations was studied by numerical methods⁴⁰ or by Monte-Carlo simulation.⁴² This last method has permitted a direct study of the transition which occurs by a nucleation process: when the system is in the lower state for C near C_s , spatial domains of higher concentration may appear as a result of fluctuations. When such a "nucleus" attains a sufficient "critical" size, instead of being damped by diffusion, it

uses diffusion to grow, and drives the system to the upper state.

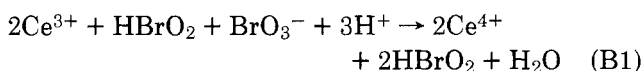
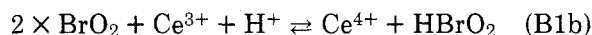
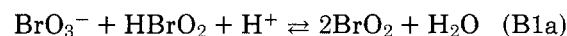
Finally, model VI⁵⁴ was proposed as a reduced model of the Belousov-Zhabotinskii reaction. It presents limit cycle type oscillations and excitability as observed experimentally. This scheme takes into account the main features of the reaction mechanism proposed by Field, Körös, and Noyes.⁵⁵ The model can be related to the complete mechanism by means of the identities $A \equiv B \equiv \text{BrO}_3^-$, $X \equiv \text{HBrO}_2$, $Y \equiv \text{Br}^-$, and $Z \equiv 2\text{Ce}^{4+}$; the stoichiometric factor f accounts for the complexity of the oxidation process of organic species.

It is important to notice that the investigation of most of the reaction schemes quoted in the previous section was generally achieved before experimental evidence of purely dissipative structures was obtained. However, quantitative description of real reactions can only be achieved through the determination of reaction mechanism. Such studies are under way, although they are not yet satisfactory, especially because most of the experimental studies do not satisfy the main thermodynamical prerequisite, the control of constraints. This is why experimental studies in continuous-flow stirred-tank reactors are so important, first to determine the phenomenological features of a given reaction, as presented above, and second to check the validity of the reaction mechanisms which are proposed. Thus, at the end, one has to relate experimental features and reaction mechanism through measured kinetic constants in order to build up a complete understanding of dissipative structures. Until now the best attempt has been made for the Belousov-Zhabotinskii reaction by Noyes and Field.^{55a} For more simplicity the main steps can be grouped in three overall processes.

Process A: reaction of bromide with bromate ion to yield bromine. This last species undergoes the fast reaction with malonic acid to generate bromomalonic acid.



Process B: autocatalytic formation of bromous acid with a rapid oxidation of Ce^{3+} to Ce^{4+} .



(54) R. J. Field and R. M. Noyes, *J. Chem. Phys.*, **60**, 1877 (1974); R. J. Field, *ibid.*, **63**, 2289 (1975).

(55) R. M. Noyes, R. J. Field, and E. Körös, *J. Am. Chem. Soc.*, **94**, 1394 (1972); R. J. Field, R. M. Noyes, and E. Körös, *ibid.*, **94**, 8649 (1972).

(55a) This Account was in press when a detailed mechanism for the reaction of Bray that satisfies a body of experimental observations was published by K. R. Sharma and R. M. Noyes, *J. Am. Chem. Soc.*, **98**, 4345 (1976).

(46) A. Nitzan, P. Ortoleva, J. Deutch, and J. Ross, *J. Chem. Phys.*, **61**, 1056 (1974).

(47) A. Lotka, *J. Phys. Chem.*, **14**, 271 (1910); *Proc. Natl. Acad. Sci. U.S.A.*, **6**, 410 (1920); *J. Am. Chem. Soc.*, **42**, 1595 (1920).

(48) A. M. Turing, *Philos. Trans. R. Soc. London, Ser. B*, **237**, 37 (1952).

(49) I. Prigogine and R. Lefever, *J. Chem. Phys.*, **48**, 795 (1968); M. Herschowitz and G. Nicolis, *ibid.*, **56**, 1890 (1972).

(50) P. Hanusse and A. Pacault, "Proceedings of the 25th International Meeting of the Société de Chimie-Physique, 1974", Elsevier, Amsterdam 1975, p. 50.

(51) B. B. Edelstein, *J. Theor. Biol.*, **29**, 57 (1970).

(52) C. Vidal, *C. R. Hebd. Acad. Sci., Ser. C*, **275**, 523 (1972); **271**, 1713 (1972).

(53) J. Boissonade, *J. Chim. Phys.*, **73**, 540 (1976).

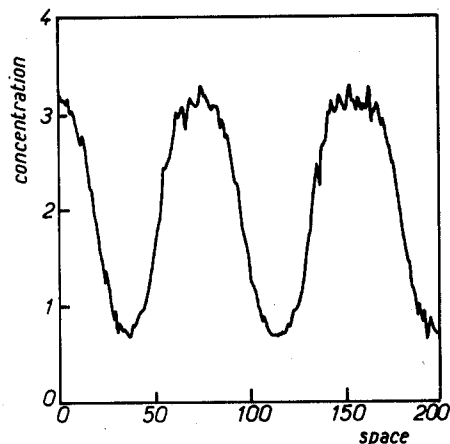
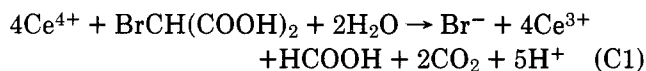


Figure 6. Fixed spatial structure (in arbitrary units).

This process is important only when $[\text{Br}^-]$ is under a critical value, bromide ion being an inhibitor of process B by step A2. There is an autocatalytic production of HBrO_2 limited by its dismutation in step B2. In process B, there is a very rapid accumulation of Ce^{4+} .

Process C is a recovery process.



This process is the Ce^{4+} oxidation of organic brominated species into formic acid and carbon dioxide and generates a bromide ion, thus switching back the reaction to process A. As process A proceeds, process C continues to deplete Ce^{4+} from the reaction mixture, enabling the bromide concentration to undergo the critical value below which process B can be switched again.

The detailed mechanism of the oxidation of organic species is still continuing to develop.⁵⁶

(56) J.-J. Jwo and R. M. Noyes, *J. Am. Chem. Soc.*, **97**, 5422 (1975); R. M. Noyes and J.-J. Jwo, *ibid.*, **97**, 5431 (1975).

The computer simulation of the complete model,⁵⁷ with most of the step rates available from experimental data, has shown a limit cycle behavior in semiquantitative agreement with experimental values.

Conclusion

Nearly a century was necessary for scientists to realize that the increase of entropy of a system could sometimes appear to be beneficial. Although this increase is an unavoidable obstacle to the maximum yield in all machines, it is the origin of a new understanding of living things. After a long controversy it has reconciled the evolution toward equilibrium of the lifeless world with living things that can undergo spatial structure and functional organization. Thermodynamics can now explain living systems if their surroundings make them develop far from equilibrium conditions, as has been argued by Prigogine.⁵⁸

There is a common feeling that complexity can give rise to new things. Nevertheless the strange phenomena discussed in this Account (multiple stable states, excitability, temporal and spatial structuration) are still amazing in view of the quite ordinary chemistry involved. Will it then be possible, as we have done, to study in detail these new phenomena and thus have solid bases for their qualitative development in other fields (biology, sociology, linguistics)⁵⁸ in which the great number of parameters make quantitative explanation difficult?

(57) D. Edelson, R. J. Field, and R. M. Noyes, *Int. J. Chem. Kinet.* **7**, 417 (1975).

(58) G. Nicolis and I. Prigogine, *Q. Rev. Biophys.*, **4**, 107 (1971); I. Prigogine, "Time, Structure and Entropy. International Study of Some Current Problems", Prague, 1971; I. Prigogine, G. Nicolis, and A. Babloyantz, *Phys. Today* (November 1972); I. Prigogine, "La naissance du temps", Communication au symposium jubilaire de l'Académie Internationale de Philosophie des Sciences, Grand-Drongen; I. Prigogine and G. Nicolis, *Theor. Phys. Biol., Proc. Int. Conf.*, 3rd, 1971, 89 (1971); G. Nicolis and J. F. G. Auchmuty, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 2748 (1974); I. Prigogine, G. Nicolis, and A. Babloyantz, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 99 (1974); I. Prigogine and I. Stengers, "Neptuniens et Vulcaniens", preprint.