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Bistable and Oscillating Chemical Reactions

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In the last decade the number and the diversity of isothermal oscillating reactions in homogeneous aqueous solution have tremendously increased. We present an updated classified review of these chemical reactions.

KEY WORDS: Nonlinear dynamics; chemical bistability; oxidoreduction reactions.

> L'impossibilité d'isoler la nomenclature de la science et la science de la nomenclature tient à ce que toute science physique est nécessairement formée de trois choses: la série des faits qui constituent la science, les idées qui les rappellent, les mots qui les expriment. Le mot doit faire naître l'idée, l'idée doit peindre le fait; ce sont trois empreintes d'un même cachet; et comme ce sont les mots qui conservent les idées et qui les transmettent, il en résulte qu'on ne peut perfectionner le langage sans perfectionner la science, ni la science sans le langage, et que quelques certains que furent les faits, quelques justes que fussent les idées qu'ils auraient fait naître, ils ne transmettraient encore que des impressions fausses, si nous n'avions pas des expressions exactes pour les rendre. [Lavoisier, *Discours préliminaire du traité élémentaire de chimie* (1789)].

1. INTRODUCTION

This epistemological conception has guided our approach to nonequilibrium dynamics in chemical systems. The use of a well-defined vocabulary that one of us initiated (A. P.) in the early 1970s and published in 1979(1) had a significant influence on the organization and the understanding of scattered facts. Appropriate experimental conditions were developed and oscillatory behaviors and different multistability phenomena were classified, thus helping to prevent the unfounded discussions that were

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still too often the case in this field in the early 1970s. In the same spirit we propose here an updated classification of oscillating reactions, whose number has tremendously increased in the last few years.

Homogeneous oscillating and isothermal chemical reactions have not only excited the curiosity of kineticists, engineers, chemists, and biochemists interested in the rythmic aspects of their evolution, but also that of numerous physicists and mathematicians who find the richness of their dynamic behavior most appealing. It has not always been that way. Before the end of the 1960s the few oscillating reactions known were regarded as mere laboratory curiosities, and more often as artifacts resulting from poorly controlled experimental conditions. A common misinterpretation of the phenomenon led to the belief that such behavior transgressed the second law of thermodynamics.

During the 1970s the number of sceptics was decreasing. Two reasons can explain this. First, the progress in the study of the thermodynamics in irreversible processes pioneered by Ilya Prigogine and the Brussels school.(2,3) They showed that some chemical systems can spontaneously develop periodic henomena in time (oscillations) and in space (spatial structures) if they have appropriate nonlinear kinetics and evolve far from their equilibrium state. The second reason was the elaboration of detailed kinetic mechanisms for the few oscillating isothermal reactions known at that time.(4-9) From a technical point of view, a decisive improvement in the study and the characterization of temporal phenomena(10,11) has been achieved by the use of continuous stirred tank reactors (CSTR).(12) In such devices the continuous supply of reagent and elimination of products make it possible to maintain the chemical reaction for as long as necessary far from its equilibrium state.

At the beginning of the 1980s an efficient and practical method was proposed(12-15) to elaborate basically different oscillating chemical reactions. The number and the variety of the reactions increased, but the majority of the oscillating reactions were still derived from halogen chemistry. The number of oscillating chemical reactions has been increasing because they are being sought out. Halogens are no longer necessary and now such reactions are known to occur with other elements of the periodic table.

2. REVIEW ON OSCILLATING AND BISTABLE CHEMICAL REACTIONS

We only consider the case of reactions in a homogeneous medium. Among them there is a traditional distinction between thermokinetic and isothermal oscillating reactions. In the former, the changes in concentration are associated with important variations in temperature and thus with changes in the rate constants. There is a strong coupling between the thermal phenomenon and the kinetic process.(16) On the contrary, in the second type of reaction this coupling is weak. Even if small oscillations in temperature can be noticed sometimes,(17) their effects on the dynamics of the reaction can be ignored.

If we admit with some authors(18) that the periodicity of the release of carbon monoxide observed in 1917 by Morgan in the dehydration reaction of formic acid by concentrated sulfuric acid resulted from heterogeneous mechanism, then the first homogeneous oscillating reaction was discovered by Bray in 1921 during his studies on the catalytic action of the iodate/iodine couple on the decomposition of hydrogen peroxide (H_2O_2).(19) Though Bray had cautiously demonstrated that this reaction presents important oscillations of iodine concentration (I_2) even in the absence of macroscopic visible oxygen release, the homogeneity of this reaction was questioned for more than 40 years. A mechanism of the reaction was first proposed by Linblad and Degn in 1967.(7) More detailed mechanisms were later proposed by Liebhafsky and his collaborators(8,20) as well as by Sharma and Noyes.(9)

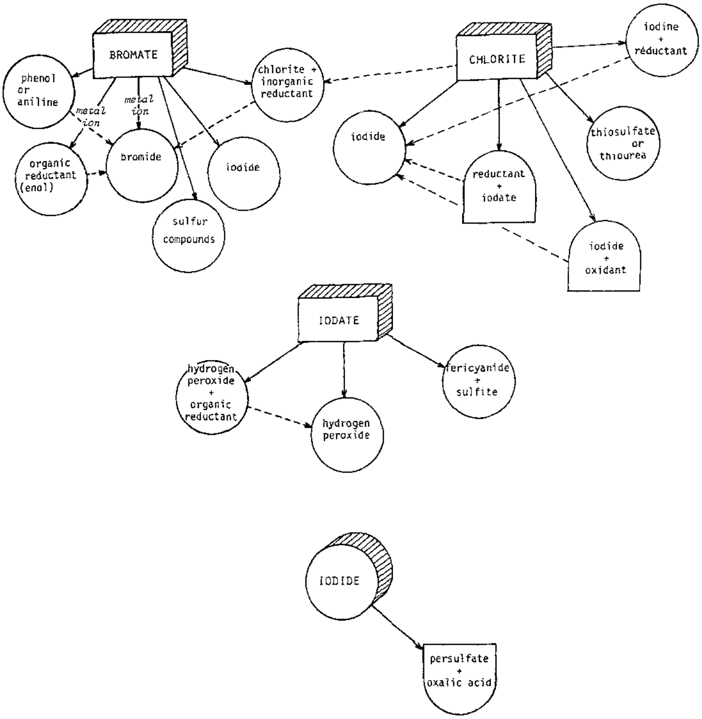
The second homogeneous oscillating reaction was discovered by Belousov, a Russian biophysicist, during his work on catalytic oxidation of the metabolites in the Krebs cycle. In 1951 he observed that the oxidation of citric acid by bromate catalyzed by cerium ions in the acid medium presented periodic changes in color from yellow [Ce(IV)] to colorless [Ce(III)]. This discovery was dimissed by his colleagues, and he could not get his results published before 1958.(21) At the beginning of the 1960s, Zhabotinskii, another Russian scientist, took over Belousov's work, replacing cerium by other metallic catalysts or metallic complex and citric acid by malonic acid, the organic substrate most commonly used nowadays. The reaction is now known as the Belousov–Zhabotinskii (BZ) reaction. The Western scientific community was made aware of this reaction during a congress in Prague in 1968. In 1972, Field *et al.*(6) presented a detailed mechanism of the reaction that could account for the oscillatory behavior in a homogeneous medium.(6) In the second half of the 1970s, thanks to studies in open reactors, the fantastic richness of behavior of oscillating reactions was revealed.(11,22)

In 1980, even though the number of research groups interested in this type of reaction has increased through out the world, the published oscillating reactions were still nothing but variants or hybrids of the two previous reactions; the next year the first chlorite oscillating reaction was discovered by De Kepper *et al.*(13) and they proposed a systematic technique to discover new oscillating reactions. It makes use of flow reactors and is based on a theoretical work developed by Boissonade.(14,15) Once this step was reached, diversification of oscillating reactions grew. As we shall see, the great majority of them are still closely linked to reduction reactions of oxyhalogen compounds.

The first two oscillating reactions that were not based on oxyhalogen chemistry were discovered by chance. They are the oscillating autoxidation reactions of benzaldehyde found by Jensen in 1983,(23) and sulfide oxidation by oxygen in the presence of methylene blue, found by Burger and Field in 1984.(24) Other nonhalogen oscillating reactions have since been discovered (Fig. 1b).(25–28)

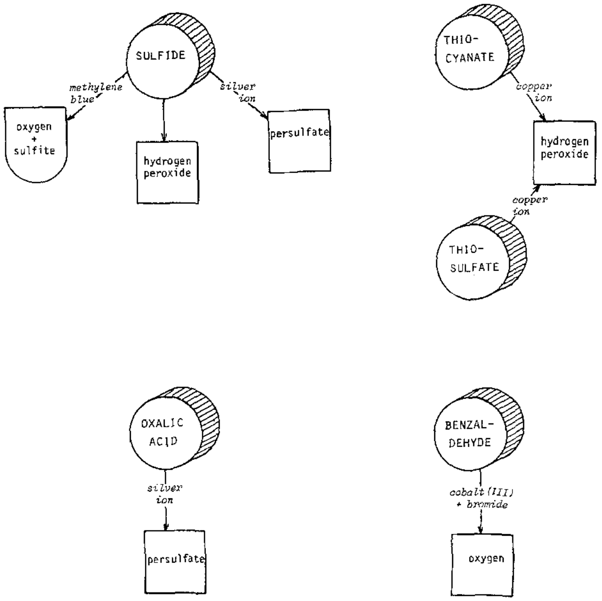
3. A CLASSIFICATION OF OSCILLATING REACTIONS

Many more or less different oscillating reactions are now known. We present in Fig. 1 a possible classification of the main oscillating systems so far discovered. Regarding the fact that the detailed kinetic mechanism of most of these reactions is still unknown, this classification is somewhat



(a)

Fig. 1a. Classification of oscillators based on the halogen chemistry.



(b)

Fig. 1b. Classification of oscillators without halogen compounds.

arbitrary. It is essentially based on the nature of the chemical elements involved. In this figure, the reactions are represented by pairs of boxes linked by a continuous line. All of them correspond to redox reactions; the reagents in the square boxes are oxidants, those in the round boxes are reducers. In some cases the boxes present a double character and correspond to a mixture of compounds. The species in the central box are regarded as compounds around which the oscillating reactions organize themselves and thus form a family. The species on the lines between the two boxes are regarded as catalysts of the reaction. The broken lines indicate that there might be simple connections between systems linked in that way.

Oscillating chemical reactions may be divided into two large categories; oscillators based on halogen chemistry and those that do not contain halogen or in which halogen does not play a central part. Note that the older oscillating reactions can show transient oscillatory behavior when performed in batch conditions, whereas most of the reactions discovered after 1980 only exhibit oscillations when performed in a flow reactor. In this latter condition nearly all the oscillating reactions also present bistability phenomena.

4. SYSTEMS WITH A HALOGEN COMPOUND

In this category, three major families appear: the bromate family, the chlorite family, and the iodate family.

4.1. The Bromate Family

4.1.1 Bromate, Bromide, Metallic Ion Reaction

This oscillating reaction has been called the minimal bromate oscillator, as it is supposed to be the core of numerous oscillating reactions in the bromate family. The catalyst can be Ce^{3+} or Mn^{2+} ions.(29,30) Before these oscillations were experimentally observed, Bar-Eli had foreseen their existence in such a system on the basis of numerical simulations of a kinetic scheme of the reaction.(31)

4.1.2. Bromate, Organic Reducer, Metallic Ion Reactions

This group of oscillating reactions contains the first oscillating reaction of the bromate family, the BZ reaction.(21,32) Since the reaction between the bromate and the organic reducing agent can produce bromide, this group is directly linked to the minimal oscillator. The metallic catalysts can be: Ce^{3+}, Mn^{2+}, $Fe(phen)_3^{2+}$, $Fe(bpy)_3^{2+}$, $Ru(phen)_3^{2+}$, $Ru(bpy)_3^{2+}$,(33) $Cr(bpy)_2^{2+}$, $Co(phen)_2^{2+}$, and $Co(bpy)_3^{2+}$.(34) The organic reducing agent commonly used is malonic acid, but other compounds have been used, such as malic acid,(35) acetylacetone,(36) ethyl acetoacetate,(37) cyclohexanone, cyclopentanone, butanone, and 3-pentanone.(38) In these systems the organic substrate plays two fundamental functions, that of a weak reducing agent and that of a bromine scavenger by the formation of brominated organic products. All of them can present transient oscillatory behavior in a closed system. In a great number of them, spatial waves have been observed.(39)

There also exists a class of systems in which the reducing agent is replaced by two substrates, each playing one of the two previous roles; the reducing part may be played by oxalic acid,(40) tartaric acid,(41,42) sugars,(43,44) and mandelic acid.(42) The partial extraction of the bromine may be provided either by a stream of inert gas (N_2) or by the bromination of acetone. In a flow reactor there is no need of providing a bromine extraction agent to obtain oscillations; the flow across the reactor is sufficient.(44)

4.1.3. Bromate, Inorganic Reducer, Metallic Ion Reactions. For the same reason as previously, this system is also linked to the minimal oscillator. Only Mn^{2+} has been used as a catalyst. The reducing agents may be SO_3^{2-}, AsO_3^{3-}, NH_2-NH_2, $H_2PO_2^-$, Sn^{2+}, or I^-.(45) Usually these reactions only oscillate when performed in a flow reactor, but if, as previously, a partial bromine extraction can be ensured, some of them may present transient oscillatory behavior in batch condition. This is the case for the BrO_3^-–$H_2PO_2^-$–Mn^{2+}–N_2 (gas)(46) and BrO_3^-–$H_2PO_2^-$–Mn^{2+}–$(CH_3)_2CO$.(44)

4.1.4. Bromate, Phenol, or Aniline Derivative Reactions. This group is known as the uncatalyzed BZ oscillators. Some of these reactions can present a limited number of oscillations in a closed system. Triggered chemical waves have been observed.(47) The basic reactions of this group are the bromate phenol and the bromate aniline systems. Orbàn and Körös(48) were the first to study systematically this class of systems and they listed a number of aniline and phenol compounds leading to oscillatory behavior. Chopin-Dumas(49) has proposed a criterion for the selection of these organic compounds and has significantly increased the number of aromatic derivatives leading to oscillating behaviors. Kinetic schemes for these reactions have been proposed.(50,51)

4.1.5. The Bromate, Iodide Reaction. This reaction(52) is more or less independent from those presented above. An interesting case of birythmicity has been studied in detail.(53) A kinetic model of the reaction has been proposed by Citri and Epstein.(54)

4.1.6. Bromate, Inorganic Reductants, Chlorite Reactions. This hybrid reaction is regarded by Orbàn and Epstein(55) as belonging to the bromate family; chlorite plays a role similar to that of the metallic ions in the 4.1.3 class. The reductants used are $Fe(CN)_6^{4-}$, H_3AsO_3, Sn^{2+}, SO_3^{2-}.

The bromate iodide–chlorite reaction also belongs to this group. It may be interpreted as resulting from a coupling between two oscillators: the bromate–iodide and the chlorite–iodide reactions. In the flow reactor its dynamical behavior is much richer than the constituent reactions.(56)

4.1.7. Bromate, Sulfur Compound Reactions. These two-component bromate oscillators were discovered by Simoyi *et al.* and are the most recent expansion of this family. Sulfur compounds may be thiocyanate,(57) thiourea,(58) and sulfide.(59) Among the three the SCN^-–BrO_3^- system is the best characterized.(57)

4.2. The Chlorite Family

4.2.1. The Chlorite Iodide Reaction. This is a basic reaction for the chlorite oscillators.(60) The chlorite iodate reductant and the chlorite iodine reductant systems are directly associated with this reaction. Epstein and Kustin(61) have proposed a detailed mechanism for this reaction.

4.2.2. Chlorite, Iodate, Reductant Reactions. The first oscillator discovered with the crossed diagram method belongs to this group(13): the ClO_2–IO_3^-–AsO_3^{3-} reaction. Besides AsO_3^{3-}, the other reducing agents are $Fe(CN)_6^{4-}$, SO_3^{2-}, $S_2O_3^{2-}$, ascorbic acid, and malonic acid.(62) Note that the ClO_2^-–IO_3^-–$S_2O_3^{2-}$ and ClO_2^-–IO_3^-–I^-–$CH_2(COOH)_2$ systems may exhibit transient oscillations in closed reactors.(63) This system can also present chemical waves similar to those observed in BZ systems.(63)

4.2.3. Chlorite, Iodine, Reductant Reactions. Iodine is reduced to iodide; thus these systems are directly linked to the chlorite–iodide system. The reducing agents leading to oscillating dynamics are $Fe(CN)_6^{4-}$, SO_3^{2-}, $S_2O_3^{2-}$.(64)

4.2.4. Chlorite, Iodide, Oxidant Reactions. Adding oxidants to the chlorite–iodide system enhances the oscillating properties of the system. The following oxidants have been used: permanganate, bichromate, and persulfate.(64) Bromate could be included among them.(56)

4.2.5. Chlorite, Thiosulfate, or Thiourea Reactions. Among the chlorite oscillators, this is the only group that does not use another halogen compound.(65,66) Their mechanism is still unknown and seems to be very complex.(67)

4.3. The Iodate Family

This family is made up of four groups.

4.3.1. The Iodate, Hydrogen Peroxide Reaction. This reaction is one of the basic reactions of the iodate family. It was studied by Bray(19) and is acknowledged as the first homogeneous oscillating reaction. The reaction can oscillate in closed reactor(19,20,68,69) and in flow reactor,(70) generally for temperature above 50°C. Kinetic mechanisms of the reaction have been proposed.(7,9,20)

4.3.2. Iodate, Hydrogen Peroxide, Organic Reductant, Metallic Ion Reactions. The addition of appropriate organic compounds and of metallic ions to Bray's reaction favors the oscillating behavior at ambient temperature and yields another group of oscillating reactions. The Briggs–Rauscher reaction (IO_3^-–H_2O_2–$CH_2(COOH)_2$–Mn^{2+}) is the best known.(71) The reaction may present in a closed system a limited number of fascinating oscillations going from deep blue (I_3^- starch complex) to golden yellow (I_2), passing through colorless (I^-). The reaction has been thoroughly studied in flow reactor in our laboratory.(10,72) A detailed mechanism of the reaction has been proposed.(73) Cerium ions have also been used as catalyst.(71,74) Malonic acid may be replaced by acetone(74) and methylmalonic acid.(75)

4.3.3. The Iodate, Ferricyanide, Sulfite Reaction. This system differs from the Bray reaction. It is though to be an $Fe(CN)_6^{4-}$-perturbed SO_3^{2-}–IO_3^- bistable reaction.(76)

4.3.4. The Iodide, Persulfate, Oxalic Acid Reaction. This system is considered as belonging directly to the iodate–iodide oscillators, but the driving mechanism is unknown.(77)

5. SYSTEMS WITH NO HALOGEN COMPOUNDS

Six groups of oscillating reactions with no halogen have been observed. Four of them belong to the sulfur chemistry; among them three are based on sulfide oxydation.

5.1. The Sulfide, Oxygen, Sulfite, Methylene Blue Reaction. This reaction, discovered by Burger and Field,(24) was the first oscillating reaction based on sulfur chemistry.

5.2. The Sulfide, Hydrogen Peroxide Reaction. This is the first hydrogen peroxide sulfur compound oscillator, and was discovered by Orbàn and Epstein.(25) As for most sulfur compound systems, little is known on its detailed mechanism.

5.3. The Sulfide, Persulfate, Silver Ion Reaction. Recently discovered by Ouyang,(28) this bistable and oscillating reaction differs from the two previous ones. It is almost insensitive to oxygen, but in contrasts the introduction of small amounts of H_2O_2 quenches its oscillatory behavior.

5.4. Thiocyanate or Thiosulfate, Hydrogen Peroxide, Copper Ion Reactions. The SCN^-–H_2O_2–Cu^{2+} system is the only halogen-free reaction that can exhibit transient oscillatory behavior in batch mode. Bistability and sustained oscillations are obtained in flow mode.(26) The $S_2O_3^{2-}$–H_2O_2–Cu^{2+} reaction produces oscillation only when performed in a flow reactor.(27) Large pH changes can be observed during oscillations, which makes it quite attractive for demonstrations when using pH indicators.

5.5. The Oxalic Acid, Persulfate, Silver Ion Reaction. As far as its chemistry is known, this reaction seems to be the simplest organic oscillator. It oscillates in a flow reactor and is among the very rare systems that do not exhibit bistability in these operating conditions.(28)

5.6. Benzadehyde, Oxygen, Cobalt Ion, Bromide Reaction. The reaction is the autoxidation of benzaldehyde by oxygen, catalysed by CO^{3+}/CO^{2+} and Br^- ion. It was discovered by Jensen in a routine test reaction for cobalt.(23) Detailed mechanisms of the reaction accounting for the observed phenomena have been proposed.(78)

6. DISCUSSION

This review clearly shows that if the space of constraints is properly explored and if the reaction is maintained far from equilibrium, one can find a good number of occurrences of chemical bistability and oscillations. Note that all these reactions are redox reactions, that all the species appearing during the reaction processes are not known, and that consequently the proposed mechanisms are often based on imagination rather than on facts. However, a description of a sufficient number of reactions can lead to a classification, such as the one proposed above, which helps to reduce the number of different objects and lead to possible generalizations. Such classifications should help in selecting the most relevant kinetic features and thus reduce the number of possible variables capable of explaining and predicting large bodies of facts. One may hope to determine in this way the pertinent fundamental mechanisms.

The two first steps, description and classification, are now being achieved. No doubt this effort will provide a better understanding of the general principles underlying these phenomena, which now look so familiar, but which seemed so strange not more than 15 years ago.

REFERENCES

1. A. Pacault, in *Synergetics. Far from Equilibrium*, A. Pacault and C. Vidal, eds.(1979), p. 128.
2. P. Glansdroff and I. Prigogine, *Structure, Stabilité et Fluctuation*, (Masson, 1971).
3. G. Nicolis and I. Prigogine, *Self-Organization in Non-Equilibrium Systems* (Wiley, New York, 1977).
4. A. M. Zhabotinskii and M. D. Korzukhin, in *Oscillating Processes in Biological and Chemical Systems*, G. M. Frank, ed. (Nauka, Moscow, 1967), p. 149.
5. A. M. Zhabotinskii, A. N. Zaikin, M. D. Korzukhin, and G. P. Kreitzer, *Kinet. Katal.* **12**:584 (1971).
6. R. J. Field, E. Körös, and R. M. Noyes, *J. Am. Chem. Soc.* **94**:8649 (1972).
7. P. Lindblad and H. Degn, *Acta Chem. Scand.* **21**:791 (1967).
8. I. Matsuzaki, T. Nakajima, and H. A. Liebhafsky, *Faraday Symp. Chem. Soc.* **1974**(9):55.
9. K. R. Sharma and R. M. Noyes, *J. Am. Chem. Soc.* **97**:202 (1975); **98**:4345 (1976).
10. A. Pacault, P. De Kepper and P. Hanusse, in *Proceeding of the 26th International Meeting*

of the Société de Chimie-Physique (1974) (Elsevier, 1975); *C. R. Acad. Sci.* **280**:157 (1975); A. Pacault, P. De Kepper, P. Hanusse, and A. Rossi, *C. R. Acad. Sci.* **281c**:215 (1975).

11. P. De Kepper, A. Rossi, and A. Pacault, *C. R. Acad. Sci.* **283c**:371 (1976); P. De Kepper and A. Pacault, *C. R. Acad. Sci.* **286c**:437 (1978).
12. J. Villermaux, *Génie de la Réaction chimique* (Lavoisier, Paris, 1982).
13. P. De Kepper, I. R. Epstein, and K. Kustin, *J. Am. Chem. Soc.* **103**:2133 (1981); P. De Kepper and J. Boissonade, *Oscillations and Travelling Waves in Chemical Systems*, R. J. Field and M. Burger, eds. (Wiley, New York, 1985), p. 223.
14. J. Boissonade, Thèse, Bordeaux (1980).
15. J. Boissonade and P. De Kepper, *J. Phys. Chem.* **84**:501 (1980).
16. J. F. Griffiths, in *Oscillations and Traveling Waves in Chemical Systems*, R. J. Field and M. Burger, eds. (Wiley, New York, 1985), p. 529.
17. C. Vidal, P. De Kepper, A. Noyau, and A. Pacault, *C. R. Acad. Sci.* **286c**:437 (1978).
18. P. G. Bowers and R. M. Noyes, in *Oscillations and Traveling Waves in Chemical Systems*, R. J. Field and M. Burger, eds. (Wiley, New York, 1985), p. 473.
19. W. C. Bray, *J. Am. Chem. Soc.* **43**:1262 (1921).
20. H. A. Liebhafsky and G. M. Roe, *Int. J. Chem. Kinet.* **11**:693 (1979).
21. B. P. Belousov, in *Sbornik. Referatov. po Radiatisionni Meditsine*, (Medgiz, Moscow, 1958), p. 145.
22. C. Vidal, J. C. Roux, A. Rossi, and S. Bachelart, *C. R. Acad. Sci. Paris* **289c**:73 (1979); J. L. Hudson, M. Hart, and D. Marinko, *J. Chem. Phys.* **71**:1601 (1979); H. L. Swinney and J. C. Roux, in *Non-Equilibrium Dynamics in Chemical Systems*, C. Vidal and A. Pacault, eds. (Springer-Verlag, 1984), p. 124.
23. J. H. Jensen, *J. Am. Chem. Soc.* **105**:2639 (1983).
24. M. Burger and R. J. Field, *Nature* **307**:720 (1984).
25. M. Orbàn and I. R. Epstein, *J. Am. Chem. Soc.* **107**:2302 (1985).
26. M. Orbàn, *J. Am. Chem. Soc.* **108**:6893 (1986).
27. M. Orbàn and I. R. Epstein, *J. Am. Chem. Soc.* **109**:101 (1987).
28. Q. Ouyang, Thesis 3ème Cycle, Bordeaux (1987); Q. Ouyang and P. De Kepper, *J. Phys. Chem.* (1987), in press.
29. M. Orbàn, P. De Kepper, and R. I. Epstein, *J. Am. Chem. Soc.* **104**:2657 (1982).
30. W. Geiseler, *J. Phys. Chem.* **86**:4394 (1982).
31. K. Bar-Eli, in *Nonlinear Phenomena in Chemical Dynamics*, C. Vidal and A. Pacault, eds. (Springer-Verlag, 1981), p. 228; K. Bar-Eli and W. Geiseler, *J. Phys. Chem.* **85**:3461 (1983).
32. A. M. Zhabotinskii, *Biofizika* **9**:306 (1964); *Dokl. Akad. Nauk SSSR* **157**:392 (1964).
33. E. Körös, M. Burger, V. Friedrich, L. Ladanyl, Z. Nagy, and M. Orbàn, *Faraday Symp. Chem. Soc.* **1974**(9):28.
34. M. Handlivoova and A. Tockstein, *Coll. Czech. Chem. Commun.* **45**:2621 (1980).
35. N. Ganapathisubramanian, R. Ramaswamy, and J. C. Kuriacose, *Proc. Indian Nat. Sci. Acad. Ser. Chem. Sci.* **89**:235 (1980).
36. P. G. Bowers, K. E. Caldwell, and D. F. Prendergast, *J. Phys. Chem.* **76**:2185 (1972).
37. L. F. Salter and J. G. Sheppard, *Int. J. Chem. Kinet.* **14**:815 (1982).
38. V. J. Farage, P. H. Stroot, and D. Janjic, *Helv. Chim. Acta* **60**:237 (1977).
39. A. N. Zaikin and A. M. Zhabotinskii, *Nature* **225**:535 (1970); A. T. Winfree, *Sci. Am.* **230**:82 (1974); in *Oscillations and Travelling Waves in Chemical Systems*, R. J. Field and M. Burger, eds. (Wiley, New York, 1985), p. 441.
40. Z. Noszticius and J. Boidiss, *Magy. Kem. Folyoirate.* **86**:2 (1979); Z. Noszticius, *Magy. Kem. Folyoirate.* **86**:330 (1979).
41. L. Adamcikova and P. Sevcik, *Coll. Czech. Chem. Commun.* **47**:2333 (1982).

42. R. P. Rastogi, K. D. S. Yadava, and P. Rastogi, *Ind. J. Chem. A* **15**:338 (1977).
43. P. Sevcik and L. Adamcikova, *J. Phys. Chem.* **89**:5178 (1985).
44. Q. Ouyang, W. Y. Tam, P. De Kepper, W. D. McCormick, Z. Noszticzius, and H. L. Swinney, *J. Phys. Chem.* **91**:2181 (1987).
45. M. Alamgir, M. Orbàn, and I. R. Epstein, *J. Phys. Chem.* **87**:3725 (1983).
46. L. Adamcikova and P. Sevcik, *Int. Chem. Kinet.* **14**:735 (1982).
47. M. Orbàn, *J. Am. Chem. Soc.* **102**:4311 (1980).
48. M. Orbàn and E. Körös, *J. Phys. Chem.* **82**:1672 (1978).
49. J. Chopin-Dumas, *J. Chim. Phys.* **78**:461 (1981); J. Chopin-Dumas and P. Richetti, in *Nonlinear Phenomena in Chemical Dynamics*, C. Vidal and A. Pacault, eds. (Springer-Verlag, 1981), p. 213.
50. P. Richetti, Thesis Bordeaux (1982).
51. M. Orbàn, E. Körös, and R. M. Noyes, *J. Phys. Chem.* **83**:3056 (1979).
52. M. Alamgir, P. De Kepper, M. Orbàn, and I. R. Epstein, *J. Am. Chem. Soc.* **105**:2641 (1983).
53. H. Khalifeh, Thesis Bordeaux (1985).
54. O. Citri and I. R. Epstein, *J. Am. Soc.* **108**:357 (1986).
55. M. Orbàn and I. R. Epstein, *J. Phys. Chem.* **87**:3212 (1983).
56. M. Alamgir and I. R. Epstein, *J. Am. Chem. Soc.* **105**:2500 (1983).
57. R. H. Simoyi, *J. Phys. Chem.* **91**:1557 (1987).
58. R. H. Simoyi and I. R. Epstein, *J. Phys. Chem.* (1987), submitted.
59. R. H. Simoyi and R. M. Noyes, preprint (1987).
60. C. E. Dateo, M. Orbàn, P. De Kepper, and I. R. Epstein, *J. Am. Chem. Soc.* **104**:504 (1982).
61. I. R. Epstein, and K. Kustin, *J. Phys. Chem.* **89**:2275 (1985).
62. M. Orbàn, P. De Kepper, I. R. Epstein, and K. Kustin, *Nature* **292**:816 (1981).
63. P. De Kepper, I. R. Epstein, K. Kustin, and M. Orbàn, *J. Phys. Chem.* **86**:170 (1982).
64. M. Orbàn, C. Dateo, P. De Kepper, and I. R. Epstein, *J. Am. Chem. Soc.* **104**:5911 (1982).
65. M. Orbàn, P. De Kepper, and I. R. Epstein, *J. Phys. Chem.* **86**:431 (1982); M. Orbàn and I. R. Epstein, *J. Phys. Chem.* **86**:3907 (1982).
66. M. Alamgir and I. R. Epstein, *Int. J. Chem. Kinet.* **17**:429 (1985).
67. I. Nagypal and I. R. Epstein, *J. Phys. Chem.* **90**:6285 (1986).
68. H. Degn, *Acta Chem. Scand.* **21**:1057 (1967); H. Degn and J. Higgins, *J. Phys. Chem.* **72**:2692 (1968).
69. J. H. Woodson and H. A. Liebhafsky, *Nature* **224**:690 (1969); I. Matsuzaki, R. Simic, and H. A. Liebhafsky, *Bull. Chem. Soc. Jpn.* **45**:3367 (1970).
70. J. Chopin-Dumas, *C. R. Sc Acad. Sci.* **287**:553 (1978).
71. T. S. Briggs and W. C. Rauscher, *J. Chem. Ed.* **50**:496 (1973).
72. P. De Kepper, Thesis Bordeaux (1978).
73. R. M. Noyes and S. D. Furrow, *J. Am. Chem. Soc.* **104**:45 (1982); P. De Kepper and I. R. Epstein, *J. Am. Chem. Soc.* **104**:49 (1982).
74. D. O. Cooke, *Int. J. Chem. Kinet.* **12**:683 (1980).
75. S. D. Furrow, *Int. J. Chem. Kinet.* **11**:131 (1981).
76. E. C. Edblow, M. Orbàn, and I. R. Epstein, *J. Am. Chem. Soc.* **108**:2826 (1986).
77. J. Chopin, J. Chopin-Dumas, and M. N. Papel, in *Non-Equilibrium Dynamics in Chemical Systems*, C. Vidal and A. Pacault, eds. (Springer-Verlag, Berlin, 1984), p. 69.
78. J. H. Jensen, M. G. Roelofs, and E. Wasserman, in *Non-Equilibrium Dynamics in Chemical Systems*, C. Vidal and A. Pacault, eds. (Springer-Verlag, 1984), p. 35; M. G. Roelofs, *J. Am. Chem. Soc.* **105**:6229 (1983).