OSCILLATIONS AND TRAVELING WAVES IN CHEMICAL SYSTEMS

OSCILLATIONS AND TRAVELING WAVES IN CHEMICAL SYSTEMS

Edited by

RICHARD J. FIELD
University of Montana

MÁRIA BURGER
L. Eötvös University, Budapest

A WILEY-INTERSCIENCE PUBLICATION
JOHN WILEY & SONS
New York • Chichester • Brisbane • Toronto • Singapore

Library of Congress Cataloging in Publication Data:

Main entry under title:
Oscillations and traveling waves in chemical systems.

"A Wiley-Interscience publication."
Bibliography: p.
Includes index.
1. Chemical reactions. 2. Belousov–Zhabotinskii reaction. 3. Oscillations. I. Field, Richard J. II. Burger, Márta.

QD502.083 1985 541.3'9 84-15382
ISBN 0-471-89384-6

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

CONTRIBUTORS

J. Boissonade, C.R.P.P., Université de Bordeaux I, Talence, France

Peter G. Bowers, Department of Chemistry, Simmons College, Boston, Massachusetts

Ernő Bujdosó, Department of Chemistry, University of Montana, Missoula, Montana; Permanent address: Department of Informatics and Science Analysis, Library of the Hungarian Academy of Sciences, Budapest, Hungary

Mária Burger, Department of Chemistry, University of Montana, Missoula, Montana; Permanent address: Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary

P. De Kepper, C.R.P.P., Université de Bordeaux I, Talence, France

David Edelson, Bell Laboratories, Murray Hill, New Jersey

Irving R. Epstein, Department of Chemistry, Brandeis University, Waltham, Massachusetts

Richard J. Field, Department of Chemistry, University of Montana, Missoula, Montana

Stanley D. Furrow, Department of Chemistry, Pennsylvania State University, Reading, Pennsylvania

Peter Gray, School of Chemistry, University of Leeds, Leeds, England

John F. Griffith, Department of Physical Chemistry, University of Leeds, Leeds, England

Richard M. Noyes, Department of Chemistry, University of Oregon, Eugene, Oregon

Miklós Orbán, Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary

Peter J. Ortoleva, Department of Chemistry, Indiana University, Bloomington, Indiana, and Geo-Chemical Research Associates, Bloomington, Indiana

Hans G. Othmer, Department of Mathematics, University of Utah, Salt Lake City, Utah

Herschel Rabitz, Department of Chemistry, Princeton University, Princeton, New Jersey

Paul Rehmus, Department of Chemistry, Stanford University, Stanford, California

John Ross, Department of Chemistry, Stanford University, Stanford, California

Alan Saul, Center for Neural Sciences, Brown University, Providence, Rhode Island

Steven L. Schmidt, Western Electric Engineering Research Laboratories, Princeton, New Jersey

Stephen K. Scott, School of Chemistry, University of Leeds, Leeds, England

Kenneth Showalter, Department of Chemistry, West Virginia University, Morgantown, West Virginia

William C. Troy, Department of Mathematics, University of Pittsburgh, Pittsburgh, Pennsylvania

John J. Tyson, Department of Biology, Virginia Polytechnic Institute and State University, Blacksburg, Virginia

A. M. Zhabotinskii, Institute of Biological Physics, Puschino, Moscow Region, USSR

Arthur T. Winfree, Department of Biological Sciences, Purdue University, West Lafayette, Indiana

PREFACE

In an oscillating chemical reaction the concentrations of catalyst and/or intermediate species undergo oscillations in time. This behavior is driven by the Gibbs-free-energy decrease of an overall chemical reaction occurring far from thermodynamic equilibrium. Diffusion of these species may couple with chemical reaction under some circumstances and lead to traveling waves (spatial inhomogeneities) of chemical activity in which their concentrations are far above or below those in the bulk of the reacting mixture. These waves often propagate in a manner reminiscent of nerve-impulse transmission.

This volume provides a comprehensive treatment of the experimental behavior of these remarkable systems. Their mechanistic interpretation and relationship to rapidly developing theories of oscillatory and related behavior in these and similar systems are also treated in detail. Beyond their very great intrinsic scientific interest and importance, this direct link between experiment and theory has helped make oscillating chemical reactions an exciting and active area of current research. Each chapter in this book is written by a person who has made fundamental contributions to the development of the subject covered. A master bibliography with titles provides a key to the literature of chemical oscillations and traveling waves.

The history of oscillations in chemical systems is long; the first example, a gas-phase system, was discovered in 1828. Its richness has increased greatly over the last two decades of intense activity. A very early theoretical suggestion of the existence of chemical reactions in which oscillations in the concentrations of intermediate species occur solely as a result of homogeneous chemical kinetics was made by A. J. Lotka in a series of papers appearing in the period 1910–1920. W. C. Bray discovered in 1921 the first liquid-phase example of such a reaction, the iodate-ion-catalyzed decomposition of hydrogen peroxide, and he recognized the connection between his and Lotka's work even though the experimental system was complicated by the evolution of oxygen. These discoveries languished for about 40 years, however. One reason for this

quiescence was the relatively low level of development at that time of methods of unraveling the mechanisms of complex chemical reactions. Another reason was the widespread, mistaken impression that the second law of thermodynamics forbids such oscillations even in systems maintained far from equilibrium. Indeed, it turns out that an important reason to study oscillating chemical reactions is to develop examples of what is possible under far-from-equilibrium circumstances.

The modern history of the study of oscillating chemical reactions in the liquid phase began in Russia in 1951, when B. P. Belousov discovered temporal oscillations in the ratio [Ce(IV)]/[Ce(III)] during the cerium-ion-catalyzed oxidation of citric acid by bromate ion. However, Belousov was not able to get his discovery published until 1958 (and then only in an obscure proceedings seen only by a very few modern workers in the field). The first English translation of Belousov's original manuscript appears in this volume, and it shows that he also knew of the traveling waves that occur in this system. A. M. Zhabotinskii continued Belousov's work, and the class of oscillatory, metal-ion-catalyzed oxidations of organic compounds by bromate ion is now referred to as the Belousov–Zhabotinskii (BZ) reaction. Zhabotinskii describes here early Russian work on the BZ reaction.

The situation was much different in the late 1960s, when the existence of the BZ reaction became well known, from what it was 45 years earlier, when Bray and Lotka made their discoveries. Methods of elucidating the mechanisms of complex chemical reactions had become quite highly developed by this time, and within a few years a basic mechanistic understanding of the BZ reaction was attained. Field treats the experimental characterization of the BZ reaction and other bromate-ion-driven oscillators as well as the current state of detailed understanding of their mechanisms. Numerical simulation and modeling techniques have been of great use in attaining this understanding, and the application of these methods, including recent work on the use of sensitivity analysis, is discussed by Edelson and Rabitz.

This increase in mechanistic sophistication was matched in the late 1960s by the development of the mathematics of oscillations and pattern formation in chemical systems. Pioneering work was done by Turing (1952) and developed thereafter by Prigogine and co-workers to a point where there was a sound theoretical framework within which to interpret oscillations as well as traveling and stationary waves in chemical systems. The current status of this body of theory is treated by Othmer (temporal oscillation) and by Ortoleva and Schmidt (waves). The direct connection between the BZ reaction and theory was made by the reduction of the BZ mechanism to a relatively tractable model that retains the essence of the chemistry. The derivation, properties, and mathematics of this model are discussed by Troy and by Tyson.

Since the late 1970s there has been a further surge of activity involving the BZ reaction as well as many other oscillating reactions and springing from several related sources. The first of these is the study of the mechanisms of previously known but not understood chemical oscillators. Thus Furrow de-

scribes the experimental characterization and current state of understanding of both Bray's hydrogen peroxide–iodate ion system (now known as the Bray–Liebhafsky (BL) reaction) and a system (known as the Briggs–Rauscher oscillator) derived from a combination of the BZ and BL reactions. Bowers and Noyes discuss the very old class of gas-evolution oscillators, which have only recently been understood in terms of the supersaturation of a gas in a liquid.

A second and most important source of activity has been the introduction of flow reactor technology. This has led to much greater experimental control over oscillating reactions as well as the appearance in them of previously unobserved nonlinear phenomena, including such things as multistability (particularly bistability), two-cycle oscillations, and aperiodic or chaotic oscillations. It is possible with the high degree of control of experimental parameters attainable in flow reactor experiments to relate experimental observations directly to the sorts of bifurcation theory discussed by Othmer, De Kepper and Boissonade, and Rehmus and Ross. Flow reactor theory, especially regarding the relationship between bistability and the appearance of oscillations, and important experimental results are covered by De Kepper and Boissonade.

A most important impact of flow reactors has resulted from their use in the systematic design of new chemical oscillators. It is important to increase the number of known chemical oscillators in order to make generalizations about the appearance and characteristics of chemical oscillations in terms of their theoretical basis. A host of new, oxyhalogen-ion-based chemical oscillators have been discovered using this technique. These, especially the large and diverse class of chlorite-ion oscillators, are discussed by Epstein and Orbán.

Finally, much recent activity has resulted from the recognition that oscillating chemical reactions may be used as prototype examples of the behaviors possible in systems governed by nonlinear dynamic laws. Such systems appear in chemistry, physics, geology, biology, and engineering. Results from the study of oscillating chemical reactions are of interest to people working in all of these fields. The connection between theory and experiment is made through mathematical models derived from the mechanisms of chemical oscillators. Ortoleva and Schmidt discuss the relationship between chemical kinetics and pattern formation. Rehmus and Ross show that chemical oscillators driven by outside periodic, quasi-periodic, or chaotic perturbations can be used to obtain information not only about chemical oscillators themselves, but also about the thermodynamic and kinetic properties of a large number of related chemical, physical, engineering, and biological systems.

The chemical oscillators that have been most widely investigated are those in the liquid phase. However, the history of homogeneous, oscillatory gas-phase reactions is longer and equally as rich. Gas-phase oscillators can be separated into isothermal and thermokinetic systems. The oscillatory oxidation of carbon monoxide was discovered in 1939 and is now the best understood isothermal system. Gray and Scott develop the history of this reaction, leading up to current studies and present understanding. The most fascinating nonisother-

mal, oscillatory gas reactions are the "cool flame" oxidations of organic vapors handled here by Griffiths. Their character was first recognized in 1938, although they were discovered very early (1817). Attempts at explanation go back 40 years, but unifying thermokinetic pictures were not drawn until 1969. These chapters, as well as those by Edelson and Rabitz, De Kepper and Boissonade, Rehmus and Ross, and Othmer will be of particular interest to chemical engineers.

Traveling waves of chemical activity are intimately connected to chemical oscillations and often appear in the same systems. Ortoleva and Schmidt discuss from a mainly theoretical viewpoint the general structure and variety of chemical waves. Showalter and Saul demonstrate their relationship to bistability within the context of a detailed experimental and theoretical analysis of a single system. The best-known and best-understood examples, however, are those that appear in modifications of the BZ reaction. The relationship of these to the chemistry of the BZ reaction is discussed by Field and by Tyson. Winfree treats their elegant geometry in two and three dimensions as well as their analogy to ideas from topology and relationship to similar pattern formation phenomena in biological systems.

This research area has grown in the last 20 years from a situation of very little activity into an exciting and productive field with many workers. Its development can be viewed as a microcosm of the development of science itself. Burger and Bujdosó present an analysis of the literature of homogeneous oscillating chemical reactions that leads to conclusions concerning the personal and scientific interactions that have been involved in its growth.

It is not possible to predict the exact course of development in this still vital research area. However, whatever the future holds will surely be built on the work described in this volume. Each chapter portrays an area of intense current activity and points out where future research and application are likely to occur.

Some things seem clear. There is much mechanistic and modeling work yet to be done with presently known chemical oscillators. Equally important will be the discovery of new oscillating reactions, especially ones not based on oxyhalogen chemistry. Nitrogen and sulfur chemistry seem reasonable places to look. A class of oxygen-driven oscillators is already on the scene (Jensen, 1983), and one of these (Burger and Field, 1984) involves sulfur chemistry.

Applications in such diverse disciplines as biology, geology, and engineering will become more important as our understanding matures. Possible applications in biological problems include the quantitative evaluation of reacting enzyme systems (such as those regulating metabolic processes), signal transmission in living organisms, and mitosis. Studies of pattern formation will be of increasing importance in both biological systems (Winfree) and geological systems (Ortoleva and Schmidt).

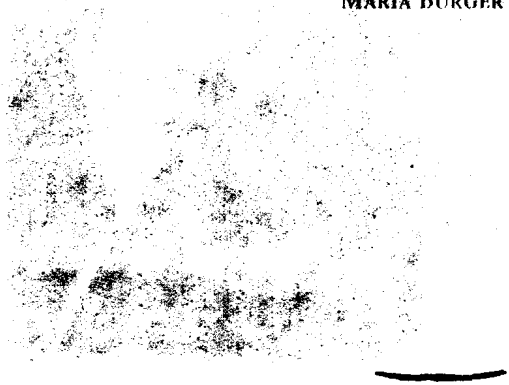
Engineering applications such as those discussed by Rehmus and Ross, Scott and Gray, and Griffiths are expected to grow rapidly. There is virtually no limit to the potential applications of the analytical and numerical methods

of analysis of ordinary and partial differential equations developed while studying oscillations and traveling waves in chemical systems. Substantial progress can be expected here in both basic theory and applications. Methods of modeling reacting chemical systems will also be greatly improved.

It seems certain that whatever directions are taken, there will be a very considerable amount of activity in the subjects of this book for a number of years.

RICHARD J. FIELD
MÁRIA BURGER

Missoula, Montana
July 1984



B. P. BELOUSOV
ca. 1950
(Courtesy of S. E. Scholl and A. Pantilov)

A. M. ZHABOTINSKII
Summer 1983
(Photo by A. T. Winfree)

CONTENTS

Introduction: The Early Period of Systematic Studies of Oscillations and Waves in Chemical Systems 1

A. M. Zhabotinskii

1 The Mathematical Aspects of Temporal Oscillations in Reacting Systems 7

Hans G. Othmer

1.1 Reaction Networks, Dynamic Systems, and Stability of Equilibrium Points, 9
1.2 Bifurcation of Time-Dependent Solutions, 24
1.3 The Dynamics of Coupled Oscillators, 45

2 Experimental and Mechanistic Characterization of Bromate-Ion-Driven Chemical Oscillations and Traveling Waves in Closed Systems 55

Richard J. Field

2.1 The Skeleton FKN Mechanism of the Classic BZ Reaction, 56
2.2 Processes *A* and *B*: Oxybromine Chemistry, 59
2.3 Stoichiometry of the BZ Reaction with Malonic Acid, 60
2.4 Organic Chemistry: The Induction Period and Process C, 62
2.5 Modeling and Simulation of the BZ Reaction, 67
2.6 Major Modifications of the Classic BZ Reaction, 69
2.7 Substitutions in the BZ Reaction, 78

2.8 Halide-Ion Additions to the BZ Reaction, 86
2.9 Physical Perturbations of the BZ Reactions, 88
2.10 Traveling and Stationary Concentration Waves, 89
2.11 Conclusion, 92

3 A Quantitative Account of Oscillations, Bistability, and Traveling Waves in the Belousov – Zhabotinskii Reaction 93

John J. Tyson

3.1 Chemistry of the BZ Reaction, 94
3.2 Simple Models of the BZ Reaction, 108
3.3 Well-Stirred Systems, 116
3.4 Unstirred Systems, 125
3.5 Conclusions, 143

4 Mathematical Analysis of the Oregonator Model of the Belousov – Zhabotinskii Reaction 145

William C. Troy

4.1 The Oregonator, 146
4.2 Temporal Oscillations, 148
4.3 A Singular Perturbation Approach to Oscillations, 151
4.4 Excitability, 156
4.5 Bursting Phenomena in Flow Systems, 157
4.6 A Spatial Model, 165

5 Chemical Oscillators Based on Iodate Ion and Hydrogen Peroxide 171

Stanley D. Furrow

5.1 Bray–Liebhafsky Oscillator, 171
5.2 Briggs–Rauscher Oscillators, 182
5.3 Comparisons of BL with BR Systems, 191

6 Numerical Techniques for Modeling and Analysis of Oscillating Reactions 193

David Edelson and Herschel Rabitz

6.1 Modeling of Temporal Systems, 195
6.2 Spatial-Temporal Systems, 201

6.3 Sensitivity Analysis, 206
6.4 Conclusion, 222

7 From Bistability to Sustained Oscillations in Homogeneous Chemical Systems in Flow Reactor Mode 223

P. De Kepper and J. Boissonade

7.1 Bistability Conditions in a CSTR, 224
7.2 From Bistability to Oscillations, 233
7.3 General Analysis, 235
7.4 Some Applications of the Cross-Shaped Phase Diagram Analysis, 241
7.5 Additional Topics, 252
7.6 Conclusion, 256

8 Halogen-Based Oscillators in a Flow Reactor 257

Irving R. Epstein and Miklós Orbán

8.1 Bromate Oscillators, 259
8.2 Chlorite Oscillators, 269
8.3 Iodate Oscillators, 280
8.4 More Complex Oscillators, 282
8.5 Mechanism and Classification, 284

9 Periodically Perturbed Chemical Systems 287

Paul Rehmus and John Ross

9.1 Quantities of Experimental and Theoretical Interest, 289
9.2 Review of Prior Work, 294
9.3 Application of Formalisms to Chemical Systems, 313

10 The Structure and Variety of Chemical Waves 333

Peter J. Ortoleva and Steven L. Schmidt

10.1 The Family of Chemical Waves, 333
10.2 Catastrophe and Propagation, 334
10.3 Waves as Perturbed Dynamic Attractors, 343
10.4 Chemical Waves as Stefan Problems, 353
10.5 Universal Behavior Near Criticality, 359

10.6 Wave–Electric Field Interactions, 367
10.7 Waves Driven by Percolation Flows, 375
10.8 Unstable Dissolution Precipitation Fronts and Liesegang Banding, 378
10.9 BZ Waves and Their Electric Field Interactions, 385

11 Propagating Reaction – Diffusion Fronts 419

Alan Saul and Kenneth Showalter

11.1 Traveling Wave Fronts, 420
11.2 Analytic Solutions, 427
11.3 Iodide Fronts in the Iodate–Arsenous Acid Reaction with Arsenous Acid in Stoichiometric Excess, 429
11.4 Higher-Velocity Fronts, 432
11.5 Iodine Fronts and Truncated Iodide Fronts in the Iodate–Arsenous Acid Reaction with Iodate in Stoichiometric Excess, 435
11.6 Summary, 437
11.7 Appendix: Stability of the Analytic Solution for Iodide Fronts with Arsenous Acid in Stoichiometric Excess, 438

12 Organizing Centers for Chemical Waves in Two and Three Dimensions 441

Arthur T. Winfree

12.1 Terms and Semantics, 441
12.2 Speculation about Pacemaker Mechanisms, 444
12.3 Pacemaker Life Histories on Videotape, 447
12.4 Organizing Centers for Chemical Waves in Two and Three Dimensions, 451
12.5 Conclusion, 467
12.6 Appendix: Undeveloped Techniques for Creating Singularities in Malonic Acid Reagent, 468

13 Gas Evolution Oscillators 473

Peter Bowers and Richard M. Noyes

13.1 Reactions from Which Oscillatory Gas Evolution Has Been Observed, 474
13.2 Experimental Features of Gas Evolution Oscillators, 478

13.3 Mechanism of the Oscillations, 483
13.4 Concluding Comments, 491

14 Isothermal Oscillations and Relaxation Ignitions in Gas-Phase Reactions: The Oxidations of Carbon Monoxide and Hydrogen 493

Peter Gray and Stephen K. Scott

14.1 Special Features of Open Systems, 496
14.2 Classical Studies of Carbon Monoxide Oxidation, 499
14.3 Modern Studies of CO Oxidation in Closed Systems, 502
14.4 Theoretical Treatments of Isothermal Oscillatory Reactions, 507
14.5 Oscillatory Ignition in the Oxidation of Hydrogen in Open Systems (CSTR), 512
14.6 Modern Studies of CO Oxidation in Open Systems (CSTR), 518
14.7 Mechanistic Interpretation of Oscillatory CO Oxidation, 522
14.8 Isothermal Oscillations in Other Systems, 527

15 Thermokinetic Oscillations in Homogeneous Gas-Phase Oxidations 529

John F. Griffiths

15.1 Survey of "Classical" Experimental Work and Its Interpretation, 531
15.2 Theoretical Background, 538
15.3 Modern Studies in Open Systems, 544
15.4 Modeling the Complexities of Hydrocarbon Combustion, 555
15.5 Conclusions, 563

16 Oscillating Chemical Reactions as an Example of the Development of a Subfield of Science 565

Mária Burger and Ernő Bujdosó

16.1 Methodology, 566
16.2 Growth of the Research Area, 566
16.3 Obsolescence of the Literature, 578

16.4 Information Flow in Homogeneous Oscillating Chemical Reactions, 579
16.5 Human Factors, 584
16.6 Conclusions, 603

Appendix: A Periodic Reaction and its Mechanism 605

B. P. Belousov

References 615

Author Index 661

Subject Index 673