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Theory and Experiments on Chemical Instabilities

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Progress is reported on experiments and theoretical studies of chemical instabilities including chemical waves, photo-illuminated thermal, chemical reactions; critical slowing down, periodic precipitation processes, resonance phenomena in oscillatory reactions, rate of entropy production in systems far from equilibrium.

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Substantial progress has been made in both experimentation and theoretical studies of chemical instabilities.

I. Experiments on Chemical Instabilities

A. Chemical Waves

We have reported in detail the first instrumentation study of chemical waves in the Belousov-Zhabotinsky reaction. Measurements are presented of velocities, amplitudes and profiles in space and time of chemical waves in this system for various temperatures, depths of solution, and in initial reactant concentrations. The measurements are made in a thin layer of a quiescent, but excitable solution by means of light absorption by ferroin, the tris (1,10-phenanthroline) ferrous sulfate complex. An extended light beam is directed through the reaction solution in a petri dish and a part of the transmitted beam is directed onto a reticon. Propagating wave profiles are recorded on this linear photodiode array with a spatial resolution of 50 . The determinations of velocity corroborate previous experimental findings. New results include

constants in the relaxation of the wave profile; trends in wave amplitude with variation of initial reactant concentrations and age of the reaction mixture; wave velocity as a function of temperature, and solution depth; and measurements of wave annihilation. Observations of additional structure include the onset of mosaic structure, that is the transition from a homogeneous to an inhomogeneous state due to the passage of the wave, and initiation spikes. The experimental verification of the constancy of velocity and profile is important for comparison with theory and for application in the important field of nerve conduction. This work has been published in the Journal of Chemical Physics (198).

B. Photo-illuminated Thermal Chemical Reactions

We have investigated the dimer-monomer equilibrium, $S_2O_6F_2 = 2SO_3F$. On illumination of this system with light absorbed by SO_3F only, multiple stationary states occur. In prior work we have measured the stable stationary states and observed chemical hysteresis. By means of an external feedback loop, in which the transmitted light is detected and that signal is fed through a delayed circuit into a device which controls the light entering the system, we can then increase the number of variables in the system such that the unstable stationary state of the original system

can be stabilized. In this way we have measured the unstable stationary state and have shown that transitions from one branch of stable stationary states to the other occur only at marginal stability points. The implication of this result is important for theory in that it shows that the effect of fluctuations, always present, is very small except at marginal stability points. It is important to emphasize that stabilization of the unstable stationary state occurs without affecting the location of the unstable stationary state in any way. In this system we have also been able to measure oscillatory states and have predicted the presence of chaos. This work has been published in the Journal of Chemical Physics (191, 193).

We have also studied extensively the photo-illuminated thermal chemical system of orthocresolpthalein, weak acid in water in the presence of a buffer. The irradiation of such systems leads to multiple stationary states and we have traced out the absence and the presence of multiple stationary states as a function of temperature and as a function of pH. Measurements are consistent with a simple theory analogous to that presented in Refs. 191, 193. We have used the technique of an external feedback loop to stabilize the unstable stationary states in this system without affecting their location in parameter space. We then proceeded to measure the relaxation from unstable stationary states in

the autonomous system to stable stationary states and measured in detail the occurrence of critical slowing down of the kinetics in the marginal stability points both within and without the region of multi-stability. This work has been written up and is being submitted shortly for publication (204, 206).

Consider the orthocresolpthalein system discussed in the previous paragraph in stationary state. By a suitable external perturbation it is possible to induce a small part of this system of one to another of the stable stationary states by means of a perturbation laser. In doing so it is possible to generate the propagation of a travelling front in the system and we measured such front propagation. Measurements are qualitatively similar to predictions of a simple theory based on reaction and diffusion. This work has been written up and is being submitted for publication (205).

C. Periodic Precipitation Processes.

Research is continuing in the area of periodic precipitation processes, also known as Liesegang rings. We have made measurements of the temporal and spatial developments of such bands, and the intervening spaces devoid of precipitate, by means of ion-specific electrodes, gravimetric analysis and absorption measurements. We have used our one-

dimensional reticon system to measure the temporal and spatial development of bands in quantitative detail. Part of this work is being written up in preparation for publication in the Journal of Chemical Physics.

D. Resonance Phenomena in Oscillatory reactions

We are studying oscillatory chemical reactions by means of external periodic perturbations. One such reaction is the combustion of acetaldehyde in the lower temperature regions (400-700^{0}K) and the other is the hydrolysis of an epoxide in aqueous solution. In the gaseous combustion system we have measured resonance responses, amplitude and change of phase throughout an entrainment band. We have made measurements in regions of frequency of external perturbation in which the system has a bi-periodic response and have analyzed that response by means of next phase maps. This technique shows that the relatively complex multi-dimensional combustion system can be reduced effectively to a one-dimensional map. This work will be written up in the next month and submitted for publication.

E. Review Article

We have written an invited review of our experimental work and part of our theoretical work which is being published in Berichte der

Bunsengesellshaft (201)

II. Theory of Chemical Instability

A. Chemical Waves

We consider propagating fronts and stationary patterns in chemical reaction-diffusion systems with nonlinear rate mechanisms maintained far from equilibrium. We study analytically and numerically the dependence on diffusion coefficients of the direction of propagation of the concentration profile which is obtained when two homogeneous steady states are placed in contact under identical constraints. We analyze the possible concentration profiles in a two-variable system with two stable stationary states for various values of diffusion coefficients and reaction time scales, and show that the direction of propagation depends on the diffusion coefficients. Finally, we show that a stationary pattern can develop behind a propagating concentration profile. We show that the pattern is very similar to that observed in our experiments on chemical waves. This work has been published in the Journal of Chemical Physics (196).

B. Periodic Precipitation Processes

1. Theory of Ostwald Ripening. The theory of Ostwald ripening is extended to include the dependence on the volume fraction of the minority

phase. The size distribution function for droplets of the minority phase and the power laws of the time dependences are derived for the late stages of phase separation. The asymptotic distribution function is found to be independent of initial conditions but does depend on the equilibrium volume fraction associated with a given quench. We show that the average radius grows as $t^{1/3}$ and the density of droplets decays as t^{-1}. The growth law and the amplitudes for these temporal power laws deviate from their values in the limit of zero volume fraction as the square root of the volume fraction. The effects of competition among droplets causes the distribution to broaden and to increase the coarsening rate. This work has been published in the Journal of Chemical Physics (190).

2. Theory of Ostwald Ripening for Open Systems. Diffusion-controlled coarsening (Ostwald ripening) of a precipitate is analyzed for the case of an open system, immersed in a reservoir of constant solute concentration. Equivalence of the evolution of such open systems and closed systems studied previously is established in the limit of infinite systems. The cause of this equivalence is screening of the bulk of the system from the reservoir by diffusive interactions between the precipitated particles. The applicability to large, but finite systems is discussed. This work has been submitted for publication in the Journal of Chemical Physics (203).

C. Rate of Entropy Production in Systems Far from Equilibrium

A suggestion has been made in the literature that an isolated system evolves in time in such a way that the rate of entropy production of the entire system is maximized along the allowed trajectory in concentration space. We investigated this suggestion and showed by some counter-examples, two theoretical arguments and one experimental case, that suggestion cannot hold generally. This work has been published in the Journal of Chemical Physics (195).

D. Review Article

We have written a review (45 printed pages) on the effect of external periodic perturbations on chemical systems including systems in stationary states, oscillatory systems and multiple periodic systems. We do not discuss the case of chaos. The review includes the topics of entrainment of oscillatory systems by external periodic perturbations, transitions from entrained to non-entrained responses, critical slowing down at such transitions, the generation of new limit cycles by suitable combinations of sinusoidal terms of external periodic perturbations, the effect of noise on such systems, and phase locking. The review has been published in a book (197).

*Starred items denote partial support credited to AFOSR

*185. "Critique of a proposed stability criterion for chemical systems far from equilibrium," Proc. Natl. Acad. Sci. 80, 3133 (1983). Claus Escher and John Ross.

*186. "Comments on two treatments of symmetry rules in chemical reactions," J. Chem. Phys. 79, 2854 (1983). Horia Metiu, George C. Schatz, and John Ross.

*187. "Path integral solutions for Fokker-Planck conditional propagators in nonequilibrium systems: Catastrophic divergences of the Onsager-Machlup-Laplace approximation," J. Chem. Phys. 79, 3765 (1983). Paul M. Hunt, Katharine L.C. Hunt, and John Ross.

*188. "Multiple ranges of flow rate with bistability and limit cycles for Schlögl's mechanism in a CSTR," J. Chem. Phys. 79, 3773 (1983). Claus Escher and John Ross.

189. "Commentary: Dissipation Regulation in Oscillatory Application to Glycolysis," *Aspects of Chemical Evolution*, G. Nicolis, Editor, John Wiley & Sons, Inc. (1984). John Ross and Peter H. Richter.

*190. "Theory of Ostwald ripening: Competitive growth and its dependence on volume fraction," J. Chem. Phys. 80, 536 (1984). J. A. Marqusee and John Ross.

*191. "Light induced bistability in $S_2O_6F_2 \rightleftharpoons 2SO_3F$: Theory and experiment," J. Chem. Phys 80, 720 (1984). E. C. Zimmermann and John Ross.

192. "Generation of multiple attractors and nonequilibrium phase transitions," J. Chem. Phys. 80, 3373 (1984). Paul Rehmus, William Vance, and John Ross.

*193. "Stabilization of unstable states and oscillatory phenomena in an illuminated thermochemical system: Theory and experiment," J. Chem. Phys. 81, 1327 (1984). E. C. Zimmermann, Mark Schell, and John Ross.

194. "Formation of Spatial Structures in Chemical Reactions," Physica 12D, 303 (1984). John Ross.

* 195. "Objections to a proposal on the rate of entropy production in systems far from equilibrium," J. Chem. Phys. 81, 4676 (1984). Bjarne Andresen, E. C. Zimmermann, and John Ross.

* 196. "Propagating and stationary structures in chemical reaction-diffusion systems," J. Chem. Phys. 82, 113 (1985). Haim Shyldkrot and John Ross.

* 197. "Periodically Perturbed Chemical Systems," in *Oscillations and Travelling Waves in Chemical Systems*, J. Field and Maria Burger, Editors, John Wiley and Sons, Inc. (1985). Paul Rehmus and John Ross.

* 198. "A quantitative study of chemical waves in the Belousov-Zhabotinsky reaction," J. Chem. Phys. 82, 1924 (1985). Peggy Marie Wood and John Ross.

199. "Reduction of dissipation in a thermal engine by means of periodic changes of external constraints," J. Chem. Phys. 82, 2453 (1985). Claus Escher and John Ross.

200. "Increased power output and resonance effects in a thermal engine driven by a first or second order model reaction," J. Chem. Phys. 82, 2457 (1985). C. Escher, A. Kloczkowski, and J. Ross.

Accepted for Publication

*201. "Non-Linearities in Chemical Reactions Temporal and Spatial Structures; Efficiency. Berichte der Bunsen-Gesellschaft ___, ____ (1985). John Ross.

202. "Marginalia", Rehovot ___, ____ (1985).

Submitted for Publication

*203. "Theory of Ostwald ripening for open systems," J. Chem. Phys., C. W. Beenakker and John Ross.

*204. "Thermochemical bistability in an illuminated liquid phase reaction," J. Phys. Chem., Jesse Kramer and John Ross.

*205. "Propagation of a chemical pulse in an illuminated thermochemical bistable system," J. Chem. Phys. Jesse Kramer and John Ross.

*206. "Stabilization of unstable states, relaxation, and critical slowing down in a bistable system," J. Chem. Phys., Jesse Kramer and John Ross.

John Ross

Professor of Chemistry

PII Redacted [redacted]

Curriculum Vitae

Field Physical Chemistry

Research Interests Theoretical and experimental studies of chemical kinetics and Instabilities

[redacted]

Education B.S., Queens College (New York), 1948
Ph.D. (Phys. Chem.) Massachusettys Institute of Technology, 1951

Experience

U. S. Army (2nd Lieutenant)	1944-46
Research Associate, Dept. of Chemistry, M.I.T.	1950-52
Research Fellow, Dept. of Chemistry, Yale	1952-53
Assistant Professor, Dept. of Chemistry, Brown	1953-57
Associate Professor, Dept. of Chemistry, Brown	1957-62
Professor, Dept. of Chemistry, Brown	1962-66
Professor, Dept. of Chemistry, M.I.T.	1966-80
Chairman, Dept. of Chemistry, M.I.T.	1966-71
Frederick G. Keyes Professor of Chemistry, M.I.T.	1971-80
Chairman of the Faculty, M.I.T.	1975-77
Professor, Dept. of Chemistry, Stanford	1980-
Professor, Dept. of Chemical Eng, Stanford (courtesy)	1983-
Chairman, Dept. of Chemistry, Stanford	1983-
Camille and Henry Dreyfus Professor of Chemistry, Stanford	1985-

John Ross - Curriculum Vitae

Awards, Societies, etc.

Eastman Fellow, M.I.T.	1949-50
NSF Postdoctoral Fellowship, Yale	1952-53
Guggenheim Fellow, Lorentz Inst., Leiden	1959-60
Alfred P. Sloan Research Fellow, Brown	1960-64
Member, American Chemical Soc., AAAS	
Fellow, American Physical Society	1964-
Fellow, American Academy of Arts and Sciences	
Visiting van der Waals Professor, University of Amsterdam	Spring 1966
Weizman Institute of Science:	1971-
Member, Executive Committe, Board of Governors	
Scientific Advisory Committee	1977-84
Chairman, Division of Physical Chemistry, American Chemical Society	1971-72
Member, National Academy of Sciences	1976
Honorary Doctorate, Weizmann Institute of Science	1984

John Ross - Curriculum Vitae

Committees

Member, Executive Committee, Division of Physical Chemistry, American Chemical Society 1961-64.

Arranged International Conference on Irreversible Thermodynamics (in honor of L. Onsager, 1962).

Member Advisory Committee of National Academy of Sciences to National Bureau of Standards, 1963-64.

Editorial Board, Annual Reviews of Physics. Chemistry, 1968-73.

Associate Editor, Journal of Chemical Physics, 1968-77.

Chairman, National Research Council, Division of Chemistry, Committee on Physical Chemistry, 1968-69.

National Research Council on Chemical Thermodynamics, 1968.

Chemistry Research Evaluation Committee of the Air Force Office of Scientific Research 1971-75.

Arranged International Centenial Boltzmann Seminar on Transport Properties, 1973.

National Science Foundation Chemistry Review Panel, 1974-77.

Advisory Committee, Energy Research and Development Administration, Ames Laboratory, Ames, Iowa. 1974-77.

Joint Faculty Committee, Harvard-M.I.T. Program in Health Sciences and Technology, 1975-77.

Standing Committee on Research of the Science and Technology Advisory Group, AFOSR 1976-79.

Member, Editorial Board, Advances in Chemical Physics, 1976- .

Committees - continued

Member, National Academy of Sciences Advisory Committee on Human Rights, 1976-1979.

Member, Environmental Pollutant Movement and Transformation Advisory Committee (EPA), 1976-79.

Member, Advisory Board of the Center for Advanced Studies, University of Virginia 1978.

Member, Department of Energy, High Energy Physics Advisory Panel, 1977-1981.

Consultant, Department of Energy, 1977-1980.

Member, Nominating Committee, American Academy of Arts and Sciences, 1978-1981.

Chairman, Air Force Advisory Committee, June 4-5, 1979.

Member, Fossil Energy Research Working Group, Department of Energy, 1979-1981.

Member, Magnetohydrodynamics Review Committee, Department of Energy, 1979.

Member, Combustion Research Facility Advisory Board, Sandia Laboratories, 1978-1981.

Editorial Advisory Board, The Journal of Physical Chemistry, 1981-1984.

Member, Board of Trustees, La Jolla Institute, 1981- .

Editorial Board, Advances in Chemical Physics, 1980-1983.

Editorial Advisory Board, Journal of Nonequilibrium

Committees (Continued)

Editorial Advisory Board, Journal of Nonequilibrium Thermodynamics, 1981.

Visiting Committees

Served on Visiting Committees to:

Clark University, Department of Chemistry, 1967

Woods Hole Oceanographic Institution, Department of Chemistry, 1972-74, Chairman

University of Minnesota, Department of Chemistry, 1967

Wesleyan University, Department of Chemistry, 1973 Chairman

University of New Hampshire, University Accreditation, 1973

State University of New York, Albany, Ph.D. Program Evaluation, 1974, Chairman

University of Minnesota, Department of Chemistry, 1975, Chairman

Dartmouth College, Department of Chemistry, 1975, Chairman

Louisiana State, Department of Higher Education, Ph.D. Program in Chemistry, 1976

University of Virginia, Dept. of Chemistry, 1976, Chairman

Visiting Committee (Continued)

Rutgers, The State University of New Jersey, Dept. of Chemistry, 1977, Chairman

Boston University, Dept. of Chemistry Board of Visitors, 1977

University of Virginia, 1981, Chairman

University of California, Irvine, 1984

Special Lectures and Lectureships

1958 Gordon Conference on High Pressures
American Chemical Society, Symposium Speaker

1960 Kirwood *Memorial Symposium*

1962 Twelfth International Solvay Congress
Boyle Lecture, University of Amsterdam

1963 Gordon Conference on Molecular Beams

1964 FMC Lectures, Princeton University
American Chemical Society, Symposium Speaker

1965 American Chemical Society Lecture Tour
Gordon Conference, Molecular Beams
Gordon Conference on Liquids

1966 Chemical Society (London)
Van der Waals Lecture, Amsterdam

1967 Pacific Northwest Lecture Series
American Chemical Society, Symposium Speaker

Lectures - Continued

1968 Enrico Fermi Summer School, Chemical Dynamics (3 lectures)
American Physical Society Symposium
Mobil Oil Research Laboratory Lecture Series

1969 Symposium on Chemical Dynamics, Pasadena

1970 American Institute of Chemical Engineers Symposium

1971 American Chemical Society Lecture Tour

1972 Solvay Congress on Membranes and Dissipative Structures
Virginia Polytechnic Institute Special Lecture Series, Chemical Engineering

1973 Chemical Lasers Conference, Gottingen
American Chemical Society Symposium on Chemical Instabilities
Gordon Conference on Theoretical Biology and Biomathematics

1974 Faraday Lectureship, Northern Illinois University
Distinguished Lectureship Series, University of Utah
Faraday Symposium on Oscillatory Phenomena

1975 Rosenstiel Lecture, Brandeis University
International Symposium on Molecular Information and Memory, Switzerland
Plenary Lecture, Australian Conference on Chemical Kinetics

1976 Plenary Lecture, Bunsengesellschaft, Germany
Gordon Conference on "Dynamical Instabilities and Fluctuations in Chemical and Quantum Systems"
Gordon Conference on "Chemical Dynamics"

Lectures - Continued

1977 Joint Physical Chemistry Seminar, California Institute of Technology, University of California, Los Angeles and University of Southern California
International Workshop on Synergetics, Germany
Sixth Canadian Conference on Theoretical Chemistry
Battelle School on Biology

1978 Distinguished Lecturers Series, University of California, Los Angeles, Department of Chemistry
International Symposium on Nonlinear Nonequilibrium Statistical Mechanics, Kyoto, Japan
International Conference on Far-from-Equilibrium Phenomena, Bordeaux, France
XVII Solvay Conference in Physics, Brussels, Belgium

1979 Wayne State University, Frontiers of Science Lecture Series, "Chemical Instabilities"

1980 IX Meeting on Statistical Physics, Mexico
University of Pittsburgh, Distinguished Lecture Series
American Chemical Society, Houston
Symposium on Biological Effects of Non-ionizing Radiation

1981 X Meeting on Statistical Physics, Mexico
Distinguished Lecture Series, Michigan State University
Distinguished Lecture Series, University of New Orleans
Reilly Lectureship in Chemistry, University of Notre Dame
National Academy of Sciences
Gordon Conference on Thermodynamics, New Hampshire
International Conference on Instabilities, Bordeaux

1982 Gordon Conference on Chemical Instabilities
American Chemical Society Symposium on Chemical Instabilities

Lectures - Continued

1983 American Chemical Society, Thermal and Chemical Engines
Los Alamos Laboratory Symposium on Fronts and Patterns
James S. Hudnall Distinguished Visiting Lecturer, University of Chicago

1984 University of California, Santa Barbara, "Structures in Chemistry"
Royal Institution, London, "Temporal and Spatial Structures"
Theoretical Chemistry Conf., Jackson Hole, Wyoming
Bordeaux Conf. "Exp't Instabilities, Efficiency of Engines"
International Conf., Toronto, "Temp. & Spatial Instabilities"
Elmau, Bunsengesellshaft, "Temp. & Spatial Instabilities, Efficiency"
Am. Inst. of Chem. Engineers, S.F., "Efficiency"