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Progress is reported in research on theory and experiments in chemical instabilities including: Thermodynamics of Chemical Systems far from Equilibrium; Critical Slowing Down Phase Relations and Dissipation in Driven Oscillatory Systems; Universal Bifurcation Structures in Driven Oscillators; Deviations from Minimum Entropy Production at Steady States of Reacting Chemical Systems Arbitrarily Close to Equilibrium; Profiles and Front Widths of Chemical Waves in the Iron-Catalyzed Belousov-Zhabotinskii Reaction; Noise in Neural Networks: Thresholds, Hysteresis, and Neuromodulation of Signal-to-Noise; and Statistical-Mechanical Theory of Many-body Effects in Reaction Rates.

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Progress is reported in experimental and theoretical chemical instabilities made since the last report dated July, 1988.

1. Thermodynamics of Chemical Systems far from Equilibrium

The critique is presented of some recent work on the relation of thermodynamics to the mass action law of kinetics, timescales in such systems and a possible need of a so-called "Extended Thermodynamics". It is shown that for most chemical reactions the thermodynamic variables change on the same timescale as the progress variable of the chemical reaction and hence there is no need for the explicit consideration of fluxes as an additional thermodynamic variable that is, so-called "Extended Thermodynamics". This article has been excepted for publication in the Journal of Physical Chemistry.

2. Critical Slowing Down Phase Relations and Dissipation in Driven Oscillatory Systems

Three dynamical properties of forced non-linear systems are discussed with approximate analytic solutions obtained from the dynamic equations for oscillatory systems, near a super critical Hopf bifurcation driven by periodic perturbations of small amplitude. With these solutions we first obtain the phase difference between the response of the system and the periodic perturbation, and its dependence on the parameters, and hence the mechanism, of the system. Second, we derive expressions for critical slowing down near edges of entrainment bands, with consideration of possible

variation of both the radius and phase of the perturbed limit cycle with the amplitude of perturbation. Third, we show by analysis the previously numerically calculated variation of the dissipation within entrainment bands, which depends linearly on the square of the amplitude of the response of the perturbed system.

3. Universal Bifurcation Structures in Driven Oscillators

We analyze an autonomous oscillatory system near a Hopf bifurcation, driven by periodic perturbations of small amplitude, by means of approximate solutions of the dynamic equations in normal form and show the existence of many new universal bifurcation structures within $p/2$ entrainment regions. The analytic results agree well with numerical solutions. This work has been submitted to Physical Review Letters.

4. Deviations from Minimum Entropy Production at Steady States of Reacting Chemical Systems Arbitrarily Close to Equilibrium

Our analysis of reacting systems displaced from equilibrium by a matter flux across the boundaries has shown that the state of minimum entropy production differs from the steady state, even in the near equilibrium regime. When the displacement δ from equilibrium is small, the derivative of the dissipation at the steady state and the dissipation itself are both of order δ^2 . The state of least dissipation is displaced from the steady state by terms of order δ^2 in the species concentrations. The theorem of minimum entropy

production may be derived by first truncating the series expansions for the reaction rates, affinities, and dissipation assuming that δ is small, and then differentiating to locate the minimum of the dissipation. This truncation procedure establishes that the dissipation is comparatively small in a neighborhood of the steady state; but it causes large relative errors in the values of the concentration derivatives and time derivatives of the dissipation within that neighborhood, because the operations of series truncation and differentiation do not necessarily commute when $\delta \neq 0$. Near the steady state, the concentration derivative of the term of order δ^3 in the dissipation is equal to or larger than the derivative of the δ^2 term. This work has been accepted for publication in *Physica*.

5. Profiles and Front Widths of Chemical Waves in the Iron-Catalyzed Belousov-Zhabotinskii Reaction

We report measurements of profiles and widths of chemical waves in the iron-catalyzed Belousov-Zhabotinskii reactions. We measure the width of the wave front at various concentrations of reactants and study waves traveling in a quiescent as well as an oscillatory medium. Two qualitatively different wave front structures are observed: waves traveling through an oscillatory medium have a steep straight front, while the waves traveling through a quiescent medium have a more gradual and bent front. Within the concentration ranges examined, no trends are observed in

the width of the wave front versus the concentration of a reactant are observed, with the exception that the full width of a wave traveling in a quiescent medium increases as the initial concentration of sodium bromate is increased. This work is being submitted to the Journal of Physical Chemistry.

6. Noise in Neural Networks: Thresholds, Hysteresis, and Neuromodulation of Signal-to-Noise.

We study a neural-network model including Gaussian noise, higher-order neuronal interactions, and neuromodulation. For a first-order network, there is a threshold in the noise level (phase transition) above which the net-work displays only disorganized behavior and critical slowing down near the noise threshold. The network can tolerate more noise if it has higher-order feedback interactions, which also lead to hysteresis and multistability in the network dynamics. The signal-to-noise ratio can be adjusted in a biological neural network by neuromodulators such as norepinephrine. Comparisons are made to experimental results and further investigations are suggested to test the effects of hysteresis and neuromodulation in pattern recognition and learning. We propose that norepinephrine may "quench" the neural patterns of activity to enhance the ability to learn details.

This work has been accepted for publication in the Proceedings of the National Academy of Sciences.

7. Statistical-Mechanical Theory of Many-body Effects in Reaction Rates

Many-body effects in reaction rates depend on the ratio, ϵ , of a rate coefficient to the product of a diffusion coefficient and a radius, and on the reduced volume fraction, ϕ_0 , of one or more reactants. We present a statistical-mechanical theory of the macroscopic kinetics (deterministic rates) of reactions in solutions, and fluctuations therefrom, for arbitrary ϵ and ϕ_0 , by deriving expressions for effective forward and reverse rate coefficients and their dependence on ϵ , ϕ_0 to lowest order. We use an enzyme-catalyzed reaction as an example. There are two corrections to rate coefficients (for $\epsilon = 0$, $\phi_0 = 0$) at a given ϵ , $\phi_0 \neq 0$, and both are proportional to $\phi_0^{1/2}$ (the square root of the total enzyme density in the example): The first is an uncorrelated screening term described by the single enzyme distribution function, which increases the rate; and the second a term described by correlations among enzymes, which decreases the rate. In the limit of very fast reactions the correlation term is negligible, and the screening term reduces to that previously obtained for diffusion controlled reactions. For other cases both terms contribute: for example in the range $\phi_0 \sim 10^{-2}$ to 10^{-1} and $\epsilon \sim 1$ to 10 the corrections vary from a few percent to 30%, as obtained from numerical solutions of the corrections for the enzyme example. We discuss a quasi-stationary state of the example and derive a generalization of the Michaelis-Menten

equation for all ε , ϕ_0 . Fluctuations from the deterministic motion are shown to be small for three-dimensional systems. This work has been submitted to the Journal of Chemical Physics for publication.

8. Listing of work in progress

Additional research is in progress on: a. experiments on relative stability in systems with multiple stationary states; b. experiments on complex reaction mechanisms in combustion; c. experiments on the temporal and spatial onset of hydro-dynamic instabilities; d. neural net-works; e. the relation of observations and characteristics of complex reactions to their mechanisms.

Invited Lectures:

Chaired Gordon Conference on Non-linear Chemistry and Oscillations and presented current research.

Research presentation to Material Science Board of Darpa

Publications:

1. "Complex Oscillations in the Combustion of Acetaldehyde"
2. "On Liapunov Functions for Reacting Systems Displaced from Equilibrium"
3. "Explicit Solutions of Normal Form of Driven Oscillatory Systems in Entrainment Bands"
4. "Thermodynamics of Chemical Systems far from Equilibrium"
5. "Critical Slowing Down, Phase Relations, and Dissipation in Driven Oscillatory Systems"

6. "Spectral Kinetics: Study of Complex Reactions by External Perturbations"

7. "Approximate Solutions of Non-linear Systems Driven with Periodic Perturbations of Arbitrary Form"

8. "Universal Bifurcation Structures in Driven Oscillators"