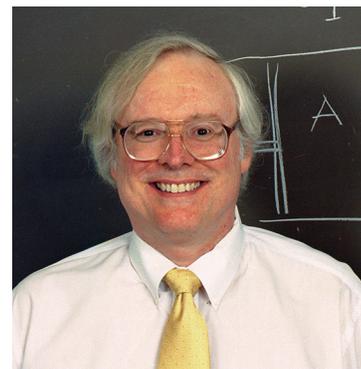


A CONTINUING RESEARCH

collaboration exists with Katharine Hunt and John Ross (Stanford). We are pursuing a global thermodynamic and stochastic theory of open chemical systems far from equilibrium. Recently, we analyzed a broad class of isothermal, multi-component reaction mechanisms with multiple steady states, studied under the assumption of local equilibrium. We generalized species-specific affinities of reaction intermediates in open systems, obtained in our prior work for non-autocatalytic reaction mechanisms, to autocatalytic kinetics and we defined with these affinities an “excess” free energy differential $d\phi$. The quantity $d\phi$ is the difference between the work required to reverse a spontaneous concentration change and the work available when the same concentration change is imposed on a system in a reference steady state. The integral of $d\phi$ is, in general, not a state function, but it is when the system exhibits detailed balance. In contrast, the function ϕ_{det} obtained by integrating $d\phi$ along deterministic kinetic trajectories is a state function, as well as an identifiable term in the time-integrated dissipation. Unlike the total integrated dissipation, ϕ_{det} remains finite during the infinite duration of the system’s relaxation to a non-equilibrium steady state, and hence ϕ_{det} can be used to characterize that process. The variational relation $d\phi \geq 0$ is a necessary and sufficient thermodynamic criterion for a stable steady state, in terms of the excess work of displacement of the intermediates, and ϕ_{det} is a Liapunov function in the domain of attraction of such steady states. An interesting connection exists between the non-equilibrium thermodynamics and stochastic theory. For equilibrating and non-autocatalytic systems, the stationary distribution of the master equation may be obtained in the form $P_S = N \exp(-\phi/kT)$. This generalizes the Einstein fluctuation formula to multivariable systems with detailed balance, far from equilibrium. Most recently, attention has centered on study of systems with stable limit cycles. Long-standing interest in molecular scattering problems continues, especially in those involving dissociative processes.



Paul M. Hunt

Nonequilibrium Thermodynamics/ Molecular Scattering

ASSOCIATE VICE PRESIDENT
FOR RESEARCH

AND

PROFESSOR

(b. 1953)

B. S., 1975,
Michigan State Univ.;

Ph.D., 1978,
Oxford Univ.;

NSF Postdoctoral Fellow, 1978-79,
Harvard Univ..

517-432-4562

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