



A Tribute to James T. (Casey) Hynes

"I have not all my facts yet but I do not think there are any insuperable difficulties. Still, it is an error to argue in front of your data. You find yourself insensibly twisting them round to fit your theories."

Sir Arthur Conan Doyle

The Reigate Puzzle

It is with great pleasure that we write this Tribute honoring Casey Hynes. While the majority of this tribute highlights Casey's contributions as a scholar and mentor, one cannot emphasize enough Casey's signal role in meetings and scientific debate, where his ability as a communicator shines bright. It is of the highest importance in the art of science to be able to recognize out of a number of facts, which are incidental and which are vital. In moments of confused scientific debate when entropy and dissipation threaten to hold sway, Casey concentrates on weaving the useful facts into a simple and intuitive physical picture. While each fact is merely suggestive in itself, together they have a cumulative force, a force that allows all to see and rationalize the facts in a different light with new, deeper understanding.

Casey's research has evolved from his early days, working on the formal theory of quantum and classical correlation functions, to his current research program with its strong emphasis on the modeling of elementary chemical processes in solution with the goal to link computational approaches to a simple, yet correct physical framework that in turn directly elucidates fundamental questions of experimental interest.

An essential step in this evolution was the pioneering development of the Grote–Hynes reaction rate theory. Since the early work of Kramers, the Langevin equation had been used extensively as a prototypical model for simple chemical and physical reaction processes that are coupled to the surrounding thermal environment. Kramers derived explicit solutions for the rate over a parabolic barrier separately in the limits of weak and strong damping based on a flux over population calculation. The major advance of the Grote–Hynes theory, using the generalized Langevin equation, was the pivotal idea that the rate constant is assumed to depend on the frequency component of the dynamical friction at the reactive frequency. Freeing the condensed phase environment from the unrealistic

confines of macroscopic Brownian motion paved the way for novel interpretations of solvent effects, as well as providing a powerful tool for calculating rate constants. This work led naturally to the successful inclusion of solvent effects in proton transfer, electron transfer, and other reaction types, and also to electronic relaxation through conical intersections, vibrational relaxation, and rotational dynamics of a variety of systems.

During the late 1980s and early 1990s, Casey undertook a series of collaborations with Kent Wilson. The resulting works intertwined the theoretical advances enabled by Grote–Hynes theory and its extensions with the computational prowess of the Wilson group in performing molecular dynamics simulations. Realistic model simulations of S_N1 and S_N2 reactions clearly demonstrated the validity of not only the Grote–Hynes theory but also the Zwan–Hynes theory of nonadiabatic solvation effects. A simulation of the vibrational relaxation of a dipolar molecule in water demonstrated the correctness of Landau–Teller theory, a theory that Casey put to good use later in his career. The incredible synergy of formal theory combined with molecular dynamics simulation, so lucidly demonstrated in these works, is a characteristic feature of many of Casey’s subsequent investigations.

Casey’s more recent work compellingly reflects that much of the insight gained in the context of thermally activated events

in solution carries over directly to the femtosecond domain. Examples range from excited-state proton transfer to hydrogen bond dynamics and water reorientation in solvation shells and the role of nonequilibrium solvation in the ultrafast events at conical intersections. Casey’s unique insight into the role of nonequilibrium phenomena in chemical dynamics has thus continued to shape the intuition of a new generation of experimentalists and theorists.

The sheer breadth of Casey’s interests, from gas-phase energy flow to heterogeneous reactions relevant to atmospheric ozone depletion, is such that an overarching tribute to each of the individual areas is not feasible here. Fortunately, our task is simplified. The contributions to this Festschrift exemplify the range and influence of Casey’s extraordinary contributions, and they provide a testament to the mark he has made on both the experimental and theoretical community to date. We wish Casey the best of success as he continues to enlighten us in the years ahead.

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Guest Editors