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### Reaction-rate theory: fifty years after Kramers

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#### ABSTRACT

The calculation of rate coefficients is a discipline of nonlinear science of importance to much of physics, chemistry, engineering, and biology. Fifty years after Kramers' seminal paper on thermally activated barrier crossing, the authors report, extend, and interpret much of our current understanding relating to theories of noise-activated escape, for which many of the notable contributions are originating from the communities both of physics and of physical chemistry. Theoretical as well as numerical approaches are discussed for single- and many-

dimensional metastable systems (including fields) in gases and condensed

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reaction-rate theory for moderate-to-strong friction; the authors

ize the physical situation and the close connection between unimolecular

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rate theory and Kramers' work for weakly damped systems. The rate theory accounting for memory friction is presented, together with a unifying theoretical approach which covers the whole regime of weak-to-moderate-to-strong friction on the same basis (turnover theory). The peculiarities of noise-activated escape in a variety of physically different metastable potential configurations is elucidated in terms of the mean-first-passage-time technique. Moreover, the role and the complexity of escape in driven systems exhibiting possibly multiple, metastable stationary nonequilibrium states is identified. At lower temperatures, quantum tunneling effects start to dominate the rate mechanism. The early quantum approaches as well as the latest quantum versions of Kramers' theory are discussed, thereby providing a description of dissipative escape events at all temperatures. In addition, an attempt is made to discuss prominent experimental work as it relates to Kramers' reaction-rate theory and to indicate the most important areas for future research in theory and experiment.

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