

Activation Energies Beyond Arrhenius

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ABSTRACT

How the dynamics of a reaction, or other chemical process, changes with temperature is one of the most fundamental measures of its behavior. This is most directly characterized by its activation energy, obtained through an Arrhenius analysis involving measurements or simulations of the dynamics at different temperatures. In this talk recently developed methods that enable the activation energy to be determined from simulations at a single temperature will be described. A key advantage of these approaches is that they enable separation of not only energetic and entropic driving forces: They also offer mechanistic insight into these driving forces through a rigorous decomposition of the activation energy into contributions associated with the different motions and interactions. This is information that is not available in any other way. These methods are providing new understanding of dynamics from diffusion to reorientation to chemical reaction to spectroscopy. Examples of the approach will be discussed in the context of the structure and dynamics of water in osmolyte solutions and diffusion of methane in zeolites.