Pressure-Dependent Rate Constant Predictions Utilizing the Inverse Laplace Transform

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Pressure-dependent reactions are ubiquitous for gas-phase chemical processes like combustion, atmospheric chemistry, and chemical vapor deposition. For proper modeling and better understanding of these processes, their pressure-dependent rate constants $k(T,p)$ need to be known or estimated. Apart from direct experimental measurements, $k(T,p)$ is obtained from microscopic balancing employing the master equation (ME) approach, using microscopic rate constants $k(E)$ as indispensable ingredient. The state-of-the-art $k(E)$ prediction is based on the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. This method, however, is limited to small molecules and requires the explicit knowledge of the transition state geometry. An alternative approach for $k(E)$ computation is the inverse Laplace Transform (ILT). This method applies to arbitrarily sized molecules and arbitrarily complex electronic structures. According to the general perception, these advantages are derogated by the low quality of $k(E)$ data obtained with the ILT approach. This lousy reputation of the ILT approach for $k(E)$ reconstruction stems from the method's high sensitivity to the input data quality. As a result, practically useless microscopic kinetic data are obtained after ILT when inaccurate or incomplete macroscopic kinetic data are provided. To redeem the reputation of $k(E)$ reconstruction via ILT, we studied various input data formats and their impact on the quality of $k(E)$ reconstruction. Our results suggest new a method for computing the $k(E)$ from well-established thermodynamics (NASA polynomials) and kinetics data formats (modified Arrhenius equations). The core idea of the method is to apply the newly-developed nonlinear models to refit the reactant's NASA polynomial and the modified Arrhenius equation and apply ILT on new fits. The computed $k(E)$ are used in the ME simulations to get an accurate and reliable estimation of $k(T, p)$. The proposed scheme could be applied to large databases like the NIST Chemical Kinetics Database.