

**Simplification of complex chemical kinetics:
what is essential?**

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S. W. Benson intended to provide “rapid and relatively quantitative estimates of thermochemical and reaction rate parameters”¹. In view of the intrinsic complexity of even the simplest “elementary” gas phase reactions, this intention today is still of practical as well as fundamental importance. This talk compares elaborate and simplified treatments of a series of basic dynamic phenomena. Collisional activation and deactivation can be described by master equations under the condition that the input parameters are well known. Simplifications may link the observables to the relevant input parameters. Falloff curves of dissociation, recombination, and complex-forming bimolecular reactions can likewise be treated by master equations. However, simplified representations^{2,3} may again provide an easier and “relatively quantitative” access to the essential input parameters. Capture processes, leading to highly excited reactive species, are governed by the interaction potential. Their rates can be determined by quantum scattering and classical trajectory calculations under the condition that the Born-Oppenheimer approximation holds. However, one meets situations where the latter is invalid such that the concept of potential energy surfaces breaks down⁴. The question arises how one could handle these cases in a simplified manner.

¹ S. W. Benson, “Thermochemical Kinetics” (2nd edn., Wiley, New York, 1976).

² J. Troe and V. G. Ushakov, Z. Phys. Chem. 228, 1 (2014).

³ J. Troe, J. Phys. Chem. A 119, 12159 (2015).

⁴ A. I. Maergoiz, E. E. Nikitin, and J. Troe, J. Chem. Phys. 141, 044302 (2014).