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Historical perspective on: RRKM reaction rate theory for transition states of any looseness [Volume 110, Issue 3, 28 September 1984, Pages 230–234]

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Summary by Rudy Marcus, Nobel prize-winner: Professor Rudolph A Marcus.

The field of unimolecular reactions and bimolecular recombination processes [1–8] has undergone a number of changes during the past 90 or so years. In the middle 1920s, the theories of Hinshelwood, Rice/Ramsperger, and Kassel were developed at a time when little was known about potential energy surfaces. So the theory was phrased in terms of the sharing of energy in a dissociating or isomerizing molecule among 'squared terms', meaning the kinetic energies and potential energies of harmonic molecular vibrations. In fact, in those early days, before the development of gas phase free radical mechanisms for unimolecular reactions, the latter were assumed to be non-free radical dissociations. They were realized, in the 1930s, to be, largely, dissociations, followed by subsequent free radical reactions. (Hinshelwood received the Nobel Prize for this free radical work.) On the theoretical side, transition state theory emerged in the mid 1930s, and in 1951–1952 I was involved in blending it and RRK theory together [9,10], resulting in what later became known as RRKM theory.

By 1951 the idea of potential energy surfaces was, of course, well known, but any accurate calculation of those surfaces was still in its infancy. In the 1951 paper the expression for the energy-dependent and angular momentum dependent microcanonical unimolecular reaction rate constant was a complicated sum [9], but by the time of the 1952 paper, I realized that by the simple expedient of interchanging the order of a summation and an integration, it could become very simple, yielding the now well-known $N^*/h\rho$ for this microcanonical rate constant [10]. In these articles we spoke of the transition state as being 'loose', or 'tight' ('rigid' it was called then), according as some of the molecular vibrations in a dissociating or isomerizing molecule had or had not become internal rotations in the transition state. Later, we treated angular-momentum conservation in a more refined way [11,12].

Variational transition state theory had been described in the literature for classical mechanical canonical and microcanonical systems [13–18]. A next step for RRKM theory was to apply this variational concept by treating the transition state in a variational way, taking into account that some of the coordinates could not be treated classically: their vibration frequencies were too high, potentially leading to errors as high as a factor of a million when many CH vibrations are involved, as I found in unpublished calculations in 1949–1951. This large effect was particularly striking in the field of mass spectrometry where unimolecularly dissociating ions were studied, as pointed out in a paper by Wolfsberg in 1962 [19] (*Cf* Friedman et al. [20]).

Some coordinates in the transition state are neither simple rotations nor simple vibrations, but rather are hindered rotations and Wardlaw and I needed a way of calculating their contribution to N^*. Typically, such coordinates were vibrations in a dissociating molecule, and became free rotations in the reaction products. Wardlaw and I classified the coordinates as being of two types: (1) vibrations that began as vibrations in the parent molecule and remained as vibrations in the transition state, and (2) vibrations in the parent molecule that became, instead, hindered or free rotations in the transition state. We termed them 'conserved' and 'transitional' coordinates, respectively. The transitional coordinates, largely hindered rotations, were treated classically using a Monte Carlo phase space computation, while the 'conserved' vibrations were treated quantum mechanically. Given some reaction coordinate, the transition state was determined as the value of that coordinate where N^* was a local minimum, a bottleneck. In Wigner's 1938 description [21] the transition state corresponded to the fewest re-crossings of the transition state by classical trajectories representing the reacting system and, hence, the least 'wasting' of the phase space of the transition state. RRKM theory assumes that all of the transition state 'hypersurface' of any given energy E and angular momentum J is equally accessible (equal *a priori* probabilities). At the same time, care was taken to treat the rotations so as to correspond to any given total angular momentum J.

The $N^*(EJ)$ was written in the CPL article as

$$N(EJ) = \int_0^{E'} N_v(E'-\varepsilon)\Omega_J(\varepsilon)d\varepsilon, \tag{1}$$

where $\Omega_J(\varepsilon)d\varepsilon$ is the number of states of the transitional modes for the given J when their total energy lies in $(\varepsilon, \varepsilon + d\varepsilon)$, and $N_v(E'-\varepsilon)$ is the number of quantum states in the conserved modes having an energy less than or equal to $E'-\varepsilon$, E' being the available energy, i.e., E minus the potential-energy minimum at the given value of

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the reaction coordinate and minus the zero-point energy of the modes included in N_v.

This articles was followed by several others with David Wardlaw, e.g., [22], and with Stephen Klippenstein, e.g., [23]. Stephen later extended the theory by introducing a 'variable reaction coordinate' method for selecting a more general reaction coordinate, a significant step forward [24,25]. Additionally, it was shown that the momentum variables in the integration over the momenta of the transitional coordinates could be treated analytically [26–29], further simplifying the problem. Both David and Stephen went on to fine careers.

A key insight into the fundamentals of transition state theory, and, hence, of the microcanonical version RRKM is given in the 1938 article by Wigner [21]. A graph of citations of that article, available in the Web of Knowledge, reveals that for the 30 years after its initial publication it was rarely cited. Then with the demonstration by computations that transition state theory in the classical domain worked well (in the case of RRKM theory, the work of the late Don Bunker demonstrated this point, e.g., [17]), and that it could be corrected by Wigner's recrossings, the citation of the 1938 paper literally exploded. A stimulating contribution to the analysis of recrossings was given by Anderson and coworkers in 1973 [30] and, I believe, helped to spur this development. Wigner's formulation [21] of transition state theory for reactions in general was an application of Liouville's theorem and the correction to transition state theory was needed when there is a recrossing of the transition state hypersurface.

Nowadays, with the aid of modern computers, the calculation of reaction rates, both unimolecular dissociations and bimolecular recombinations, has become a fine art, a far cry from the early days of the mid 1920s and the later days of the 1950s. It is a pleasure to have this opportunity to briefly recall this history of a field, as well as to thank several granting agencies, ONR, ARO and NSF for the support of the author's research.

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