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FEATURE ARTICLE

Master Equation Methods in Gas Phase Chemical Kinetics

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In this article, we discuss the application of master equation methods to problems in gas phase chemical kinetics. The focus is on reactions that take place over multiple, interconnected potential wells and on the dissociation of weakly bound free radicals. These problems are of paramount importance in combustion chemistry. To illustrate specific points, we draw on our experience with reactions we have studied previously.

Introduction

In applications of chemical kinetics, such as combustion, atmospheric chemistry, and chemical vapor deposition, chemical reactions are rarely of the type encountered in textbooks. More frequently, they are complicated processes that take place over multiple, interconnected potential wells. In combustion, the field with which we are most familiar, such reactions completely dominate our understanding of how aromatic compounds, polycyclic aromatic compounds (PAH), and soot are formed in flames.[1−7] They are the critical steps in NO_x control strategies,[8−17] and they play an important role in sulfur chemistry.[18−21] They are also pivotal in predicting the chemistry of low-temperature oxidation, cool flames, and engine knock.[22−26] Such reactions may be bimolecular (i.e., chemically activated), or they may be thermal dissociation/isomerization processes. Some of the former are "collisionless" in that the intermediate complexes are so short-lived that they effectively do not suffer any collisions under conditions that are normally of interest. However, intermediate complexes more commonly live long enough to suffer numerous collisions. In such cases, any of a number of stabilized or bimolecular products may result. These reactions (unimolecular or bimolecular), which dominate virtually all applications of chemical kinetics, require a theoretical description in terms of a time-dependent, multiple-well master equation (ME).

In the pages that follow, we discuss not only the formulation and solution of the multiple-well master equation but also the systematic procedure we have developed over the past few years for determining phenomenological rate coefficients from such solutions. Of course, it is these rate coefficients as a function of temperature and pressure, $k(T,p)$, that are required for modeling the macroscopic phenomena of interest. The methodology discussed below for multiple-well problems is restricted to one-dimensional MEs in which the total rotational−vibrational energy, E, is the independent variable. However, there are two special cases for which we can solve a two-dimensional master equation with E and J, the total angular momentum quantum number, as independent variables. The first of these cases is the collisionless (or zero-pressure) limit for any multiple-well problem; the second is the irreversible, single-well (but multiple product channel) dissociation (or isomerization) of a molecule. These special cases provide us with a means for evaluating when angular momentum conservation is likely to be important. However, more importantly, both cases are directly applicable to a wide range of important problems. Of particular importance in combustion is the dissociation of weakly bound free radicals. In the present article, we discuss our solutions to these two problems as well as the general multiple-well methodology.

Considerable confusion exists concerning the theoretical description of chemical reactions of the type that concern us in this article, reactions that inherently involve nonequilibrium state distributions. Most of this confusion stems from the failure to make a distinction between a rate coefficient and what might best be called a "flux coefficient". A flux coefficient is exactly what the name implies: for first-order processes, the product of a flux coefficient and the reactant concentration gives the flux from one molecular configuration to another. For such processes, the flux coefficient is the probability per unit time of the reactant making a transformation to the product. A rate coefficient cannot (in general) be interpreted in this way. All differences between the two are connected with weak energy-transferring collisions, either in the reactant, the product, or in an intermediate complex. A succinct, lucid, and insightful discussion of the differences between these two rate parameters (and others) is given in a seminal article written by Widom over 40 years ago.[27] What we call a flux coefficient is the rate coefficient "*r*" in Widom's paper, although we use the term somewhat more generally than Widom does (the term flux coefficient appears to have originated with Aguda and Pritchard[28]). One goal of the present article is to illustrate with some specific examples the pitfalls and flawed conclusions that can

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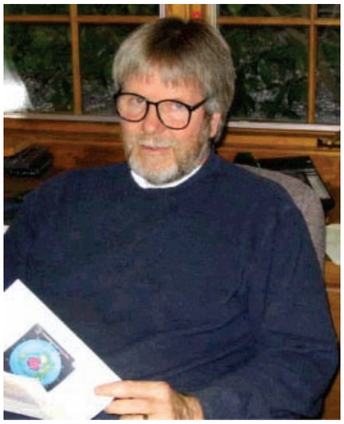

James A. Miller was born in Huntington, WV. He received his bachelor's degree from the University of Cincinnati and his Ph.D. from Cornell University in 1974. He has worked at Sandia National Laboratories in Livermore, CA, since that time. He was part of the founding staff of the Combustion Research Facility in 1980 and has had the title "Distinguished Member of the Technical Staff" since 1989. His research interests are principally in combustion chemistry and theoretical chemical kinetics. He has published extensively in both the physical chemistry and combustion literature. He is best known for his work on the nitrogen chemistry of combustion and the gas phase chemistry leading to soot formation. His paper "Mechanism and Modeling of Nitrogen Chemistry in Combustion" (Miller, J. A.; Bowman, C. T. *Prog. Energy Combust. Sci.* **1989**, *15*, 287−338) is the single most cited paper ever to appear in any combustion journal. His 1992 paper "Kinetic and Thermodynamic Issues in the Formation of Aromatic Compounds in Flames of Aliphatic Fuels" (Miller, J. A.; Melius, C. F. *Combust. Flame* **1992**, *91*, 21−39) is the most cited paper to appear in the journal *Combustion and Flame* in its 49-year history. He is a Fellow of the American Physical Society and a member of the American Chemical Society, the American Association for the Advancement of Science, and The Combustion Institute, from whom he received the Silver Medal in 1990 and the Lewis Gold Medal in 2006. He has been married to Connie Miller since 1971. They have two children, Abigail and Nathan, both of whom are budding scientists.

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occur when one does not make the proper distinctions. This approach also serves to illustrate the power of the methods described in the present article.

The mathematical development below is presented using Dirac notation. For those who are not familiar with this notation, in the present context, one can simply assume that the ket $|\mathbf{v}\rangle$ represents a column vector and that the bra $\langle\mathbf{v}|$ represents a row vector. With this small difference, everything else is the same as in ordinary matrix algebra.

Formulation of the Multiple-Well Master Equation

In the present context, the most primitive form of the master equation can be written as

$$\frac{\mathrm{d}n_i(t)}{\mathrm{d}t} = \sum_j (p_{ij}n_j(t) - p_{ji}n_i(t)) \tag{1}$$

where $n_i(t)$ is the probability of finding the system (molecule) in state i at time t and p_{ij} is the probability per unit time of a transition from state j to state i. If we deal with a large ensemble of molecules, we can regard $n_i(t)$ as a number density or population. The master equation, eq 1, is a stochastic differential equation of the "Markov" type describing the time evolution of the populations, $n_i(t)$. Pilling and Robertson[18] discuss its place in the theory of stochastic processes, where it is called the "forward equation", and its relationship to the Chapman−Kolmogorov equation. We shall not repeat that discussion here. We only note that eq 1 is Markovian because the p_{ij}'s do not depend explicitly on the time or past history of the populations. Such a model is applicable to the problems of interest to us as long as the characteristic times for intramolecular motion are much smaller than the time between collisions. This is always the case for dilute gases, and we can apply the model with impunity to any problem that interests us.

Equation 1 is also sometimes called the Pauli equation or the Pauli master equation.[29] Wolfgang Pauli,[30] in 1928, derived an equation of the same form as eq 1 from the Schrodinger equation describing the time evolution of a many-body system. Pauli's equation is valid under conditions that require the microscopic processes underlying the transition probabilities, p_{ij}, to be chaotic, thus making the equation itself Markovian. Consequently, the master equation, the Pauli equation, and the forward equation are really all the same entity.

The populations, $n_i(t)$, in eq 1 generally refer to quantum states, or at least to small numbers of quantum states. However, in principle, any linear system of first-order rate equations is of the form given by eq 1 and could be called a master equation. This appears to be the spirit in which the term is used in treating problems involving atomic clusters, peptides, and proteins.[31−33]

In molecules other than diatomics, there are too many states at energies of interest to resolve them all. Since we are primarily interested in fairly large, polyatomic molecules (or collision complexes), it is necessary to adopt a contracted, coarse-grained description of these molecular systems. Instead of solving a master equation for the populations of individual states, we formulate our ME in terms of populations of states with energies between E and $E + \mathrm{d}E$, or populations of states with energies between E and $E + \mathrm{d}E$ *and* with a total angular momentum quantum number equal to J. A subtle consequence of this contracted description is that it forces the RRKM approximation on us. The RRKM approximation is equivalent to the assumption of microcanonical, J-resolved equilibrium in the reacting complex; it distinguishes the reactivity of states only by the good constants of the motion in the isolated molecule (or complex), the total energy and the total angular momentum. Quite frequently, states are distinguished only by their total energy.

Generally, the transition probabilities appearing in eq 1 are of only two types, reactive and collisional. In astrophysical problems, radiative processes can also be significant, but they are negligible for applications that interest us here. To be concrete about the problem definition, we envision an experimental situation in which we are trying to measure the rate coefficient and product distribution for the reaction

$$\mathrm{R} + \mathrm{m} \rightleftarrows \text{products}$$

where the reactants m and R are heavily diluted in a bath of the inert gas B. Moreover, as is commonly the case in such experiments, we assume that one of the reactants, m, is maintained at a concentration that is in great excess over that of the other, R, thus rendering the reaction pseudo-first-order in n_R, the number density (or concentration) of R. Thus the following inequality holds:

$$n_\mathrm{B} \gg n_\mathrm{m} \gg n_\mathrm{R} \qquad (2)$$

where n_B is the number density of the inert diluent and n_m is that for the "excess" reactant. Typically, R is a radical and m is a molecule, but the analysis below applies regardless of the nature of R and m. The master equation for such conditions is linear and can be written as

$$\frac{\mathrm{d}n_i(E,J)}{\mathrm{d}t} = Z_i \sum_{J'} \int_{E_{0_i}}^{\infty} P_i(E,J;E',J')\, n_i(E',J')\, \mathrm{d}E' - Z_i n_i(E,J) - \sum_{j\neq i}^{M} k_{ji}(E,J)\, n_i(E,J) + \sum_{j\neq i}^{M} k_{ij}(E,J)\, n_j(E,J) - k_{\mathrm{d}_i}(E,J)\, n_i(E,J) + k_{\mathrm{a}_i}(E,J)\, n_\mathrm{R} n_\mathrm{m} \rho_\mathrm{Rm}(E,J) \mathrm{e}^{-\beta E}/Q_\mathrm{Rm} - \sum_{p=1}^{N_p} k_{p_i}(E,J)\, n_i(E,J) \qquad i = I, ..., M \quad (3a)$$

In eq 3a, $n_i(E,J)\,\mathrm{d}E$ is the concentration of isomer i of the complex (corresponding to the ith well of the potential) with an energy between E and $E + \mathrm{d}E$ and with angular momentum quantum number J; Z_i is the collision rate of complex i with the diluent molecules; E_{0_i} is the ground-state energy of isomer i; $P_i(E,J;E',J')$ is the probability that a collision will transfer a molecule in well i from a state with an energy between E' and $E' + \mathrm{d}E'$ and with angular momentum quantum number J' to a state with an energy between E and $E + \mathrm{d}E$ and angular momentum quantum number J; $k_{ij}(E,J)$ is the unimolecular rate coefficient for isomerization from well j to well i; k_{d_i} is the rate coefficient for dissociation of isomer i to the reactants m and R; $k_{p_i}(E,J)$ is the analogous rate coefficient for dissociation from well i to a set of bimolecular products, p; N_p is the number of such sets of products; M is the number of wells; $k_{\mathrm{a}_i}(E,J)$ is the association rate coefficient for the formation of isomer i from the reactants; $Q_\mathrm{Rm}(T)$ is the reactant partition function (including relative translational motion); $\rho_\mathrm{Rm}(E,J)$ is the corresponding, J-resolved density of states; and $\beta = (k_\mathrm{B}T)^{-1}$, where k_B is Boltzmann's constant. In principle, one should also include terms in eq 3a that describe reassociation of the bimolecular products. We discuss such a formulation for the general case below. However, in practice, we neglect these terms, and consequently, we do not include them in eq 3a or the equations that follow.

We can cast eq 3a in a more usable form by applying microscopic reversibility to the R + m $\rightleftarrows$ i reaction, thus replacing $k_{\mathrm{a}_i}(E,J)\, \rho_\mathrm{Rm}(E,J)\mathrm{e}^{-\beta E}/Q_\mathrm{Rm}(T)$ by $K_{\mathrm{eq}_i}(T)\, k_{\mathrm{d}_i}(E,J)\, F_i(E,J)$, where $K_{\mathrm{eq}_i}(T)$ is the equilibrium constant for the R + m $\rightleftarrows$ i association reaction and $F_i(E,J)$ is the equilibrium population distribution in well i at temperature T

$$F_i(E,J) = \rho_i(E,J)\mathrm{e}^{-\beta E}/Q_i(T) \qquad (4)$$

In eq 4, $Q_i(T)$ is the vibrational−rotational partition function for the ith well and $\rho_i(E,J)$ is the corresponding J-resolved density of states. The ME becomes

$$\frac{\mathrm{d}n_i(E,J)}{\mathrm{d}t} = Z_i \sum_{J'} \int_{E_{0_i}}^{\infty} P_i(E,J;E',J')\, n_i(E',J')\, \mathrm{d}E' - Z_i n_i(E,J) - \sum_{j\neq i}^{M} k_{ji}(E,J)\, n_i(E,J) + \sum_{j\neq i}^{M} k_{ij}(E,J)\, n_j(E,J) - k_{\mathrm{d}_i}(E,J)\, n_i(E,J) + K_{\mathrm{eq}_i} k_{\mathrm{d}_i}(E,J)\, F_i(E,J) n_\mathrm{R} n_\mathrm{m} - \sum_{p=1}^{N_p} k_{p_i}(E,J)\, n_i(E,J) \qquad i = I, ..., M \quad (3b)$$

Both forms of the association rate term in the master equation assume that the reactants, m and R, are maintained in thermal equilibrium with the bath gas throughout the course of the reaction. The form shown in eq 3b has the advantage that it does not require the explicit calculation of $\rho_\mathrm{Rm}(E,J)$, which is a complicated convolution of the state densities of the two fragments R and m. Nevertheless, we utilize both formulations in the discussion below. In chemical kinetics problems, it is common to use the one-dimensional form of eq 3b in which E is the only independent variable, rather than the two-dimensional formulation in terms of both E and J. This is an enormous simplification. It is useful to write out the one-dimensional ME for clarity:

$$\frac{\mathrm{d}n_i(E)}{\mathrm{d}t} = Z_i \int_{E_{0_i}}^{\infty} P_i(E,E')\, n_i(E')\, \mathrm{d}E' - Z_i n_i(E) - \sum_{j\neq i}^{M} k_{ji}(E)\, n_i(E) + \sum_{j\neq i}^{M} k_{ij}(E)\, n_j(E) - k_{\mathrm{d}_i}(E)\, n_i(E) + K_{\mathrm{eq}i} k_{\mathrm{d}_i}(E)\, F_i(E) n_\mathrm{R} n_\mathrm{m} - \sum_{p=1}^{N_p} k_{p_i}(E)\, n_i(E) \qquad i = I, ..., M \quad (3c)$$

The second of the inequalities (2) implies that n_m = constant, thus "linearizing" the master equation. Consequently, we need only to add a rate equation for $n_\mathrm{R}(t)$ in order to close the system. Again assuming that the reactants are always in thermal equilibrium with the bath gas, we can write such an equation in the following form:

$$\frac{\mathrm{d}n_\mathrm{R}}{\mathrm{d}t} = \sum_{i=I}^{M} \int_{E_{0_i}}^{\infty} k_{\mathrm{d}_i}(E)\, n_i(E)\, \mathrm{d}E - n_\mathrm{R} n_\mathrm{m} \sum_{i=I}^{M} K_{\mathrm{eq}_i} \int_{E_{0_i}}^{\infty} k_{\mathrm{d}_i}(E)\, F_i(E)\, \mathrm{d}E \qquad (5)$$

We should note that the assumption of thermal equilibrium for the reactants is not very restrictive. All combustion, atmospheric-chemistry, and chemical-vapor-deposition modeling makes this assumption, and experiment suggests that it is accurate. The form of the rate equation for $n_R(t)$ given in eq 5 is one-dimensional; the extension to two dimensions should be straightforward. Equations 3 and 5 constitute a set of $M + 1$ integro-differential equations for the unknown populations, $n_i(E)$ and n_R in the one-dimensional case. Except for the analysis of the collisionless limit given below, unless noted explicitly, we limit the remainder of our discussion of multiple-well problems to the one-dimensional case.

The form of the collisional energy transfer term in eq 3c implies two assumptions: (1) that any rate coefficient for energy transfer is factorable into a collision rate, $Z(E')$, and a probability density function, $P(E,E')$, (2) and that $Z(E') = Z$, a constant independent of energy.

These assumptions are not restrictive as long as the value of Z is sufficiently large and as long as Z and $P(E,E')$ are chosen consistently; that is, one must define a collision the same way in calculating both of these two quantities.[34−38] It is common practice to take Z to be Z_{LJ}, the Lennard-Jones collision rate. Such a choice is probably sufficiently accurate for weak colliders (atoms and diatomic molecules), but it fails miserably for large molecules and molecules with permanent dipole moments.[39−41] We have taken $Z = Z_{LJ}$ in all our work to date. This choice facilitates comparison of our derived or assumed energy transfer parameters with those of other workers, who virtually always assume $Z = Z_{LJ}$ — the Lennard-Jones collision rate has become a de facto standard.

Similarly, it is common practice in master equation modeling to assume a single-exponential-down function for $P(E,E')$, in which

$$P(E,E') = \frac{1}{C_N(E')}\exp(-\Delta E/\alpha), \quad E \leq E' \tag{6}$$

where $C_N(E')$ is a normalization constant and $\Delta E = E' - E$. The activating wing of $P(E,E')$ is determined from detailed balance. The use of eq 6 for $P(E,E')$ is simply a matter of convenience: the parameter α is equal to $\langle \Delta E_d \rangle$, the average energy transferred in a deactivating collision, as long as $E' \gg \alpha$. However, it is fairly clear now, both from classical trajectory calculations and from experiments that $P(E,E')$ is more accurately represented as a biexponential or some other function with a long tail. Thermal dissociation/recombination rate coefficients are not very sensitive to the form of $P(E,E')$, just to $\langle \Delta E_d \rangle$ or $\langle \Delta E \rangle$, the average energy transferred in all collisions. This may not be the case, however, for bimolecular reactions over potential wells, particularly those for which potential energy barriers to isomerization or fragmentation to bimolecular products lie much lower in energy than the reactants. An encumbrance to using more complicated (and accurate) $P(E,E')$ functions is that more parameters must be assigned in these cases, and there are no systematic procedures available for assigning them in general. Consequently, the single-exponential-down model for $P(E,E')$ is used almost exclusively in master equation modeling, with α being a function of temperature, or temperature and energy, in some cases.

Our master equation model requires rate coefficients, $k(E,J)$ or $k(E)$, for all the various isomerization and dissociation/recombination processes involved in the reaction. These rate coefficients in turn require accurate information about the potential energy surface (PES). Discussing electronic-structure methodology would take us too far afield, so we shall not do that here. The methods employed for any particular application are discussed in our papers on those applications.[42−58] Values of $k(E,J)$ are determined from the PES using transition-state theory (TST), usually conventional TST for isomerization and variational TST for dissociation/recombination reactions, whether the latter have an intrinsic barrier or not. Again, the precise methodology can vary from application to application, and it is best to consult specific articles for details of the methods employed.[42−58]

There is a subtle, but important, point to be made about the transition probabilities, p_{ij}, and rate coefficients, including $k_{a_i}n_m$ and $ZP(E,J;E',J')$, that appear in the master equations given above. These parameters are in fact flux coefficients. They are computed on a microscopic level as fluxes from one state to another, or from one set of states to another. They can be interpreted unambiguously as the probabilities per unit time of making the indicated transitions. This is in sharp contrast to the phenomenological rate coefficients that we derive below from the master equation. In this latter case, to obtain unambiguous results, one must appeal to the fundamental definition of a rate coefficient in terms of the time evolution of the species concentrations in a closed system. In general, this is a fundamental distinction between the microscopic master equation and an arbitrary system of phenomenological rate equations. One should be aware that application of the steady-state approximation to the master equation (i.e., seeking solutions to a *time-independent* master equation) is virtually always an attempt to equate a phenomenological rate coefficient to a flux coefficient. Sometimes this is a valid approach, and sometimes it is not.

Solving the Master Equation and Obtaining Phenomenological Rate Coefficients from Its Solution

The Limiting Cases. The master equation has been formulated and solved many times in the past in a number of different ways (the articles by Fernandez-Ramos et al.[59] and Pilling and Robertson[10] give extensive lists of references). There even have been several attempts to solve the two-dimensional ME in some special cases.[60−66] However, as noted in the Introduction, we restrict our attention in this article, for the most part, to the one-dimensional problem. Nevertheless, for bimolecular reactions involving potential wells, there is an important case for which one can solve the 2-D ME almost as easily as the 1-D problem. That case is the collisionless (or zero-pressure) limit, obtained by taking the limit $Z \rightarrow 0$ in the master equation. Many important reactions actually occur under nearly collisionless conditions in practical applications, particularly reactions that involve a relatively small number of atoms and relatively shallow wells. The classic example is the reaction between NH_2 and NO.[57,67] Moreover, since in the absence of collisions, J is a good constant of the motion during the entire course of the reaction, comparing 2-D solutions of the ME with their 1-D counterparts might be expected to give the maximum effect of angular momentum conservation on the thermal rate coefficients.

In the paper by Hahn et al.,[54] we derived general expressions for $|k_0\rangle$, the vector (in Dirac notation) of rate coefficients for producing the various sets of bimolecular products in the absence of collisions. This derivation is a generalization of that originally given by Miller, Parrish, and Brown.[68] We summarize the results here. If one takes the limit $Z \rightarrow 0$ in eq 3a, the resulting equation can be written in the vector form

$$\frac{d|n(E,J)\rangle}{dt} = -K(E,J)|n(E,J)\rangle + n_R n_m |b(E,J)\rangle \rho_{Rm}(E,J)e^{-\beta E}/Q_{Rm} \tag{7}$$

where $|n(E,J)\rangle$ is the vector of population densities for given values of E and J, that is, each component of the vector consists of the population of a different well at the particular E and J

values under consideration. The elements of the matrix $K(E,J)$ are algebraic sums of isomerization and dissociation rate coefficients; its diagonal entries are all positive, and its off-diagonal entries are all negative. The $|b(E,J)\rangle$ vector contains all of the association rate coefficients (microcanonical, J-resolved). Applying the steady-state approximation to eq 7, solving for $|n(E,J)\rangle$, and substituting into the equation describing the rate of formation of bimolecular products,

$$\frac{\mathrm{d}|P(E,J)\rangle}{\mathrm{d}t} = D(E,J)|n(E,J)\rangle \tag{8}$$

one obtains an expression for the rate of formation of the products,

$$\frac{\mathrm{d}|P(E,J)\rangle}{\mathrm{d}t} = D(E,J)\, K^{-1}(E,J)|b(E,J)\rangle n_{\mathrm{R}} n_{\mathrm{m}} \rho_{\mathrm{Rm}}(E,J) \mathrm{e}^{-\beta E}/Q_{\mathrm{Rm}}(T) \tag{9}$$

In equations 8 and 9, the components of $|P(E,J)\rangle$ are the number densities per unit energy of the different sets of bimolecular products, $K^{-1}(E,J)$ is the inverse of the $K(E,J)$ matrix, and $D(E,J)$ is the matrix whose i, j element is the dissociation rate coefficient from well j to product i. Note that $D(E,J)$, $K(E,J)$, and $|b(E,J)\rangle$ can be very sparse, because not every well is directly connected to every other well, and any particular well need not be directly connected to the reactants or any particular set of products.

If one integrates eq 9 over E and sums over J, the vector of thermal rate coefficients is easily identified as the factor multiplying $n_{\mathrm{R}} n_{\mathrm{m}}$

$$|k_0(T)\rangle = \frac{1}{Q_{\mathrm{Rm}}(T)} \sum_J (2J+1) \int_0^\infty D(E,J)\, K^{-1}(E,J)|b(E,J)\rangle \rho_{\mathrm{Rm}}(E,J) \mathrm{e}^{-\beta E}\, \mathrm{d}E \tag{10a}$$

One can go one step further and eliminate the troublesome density of states, $\rho_{\mathrm{Rm}}(E,J)$, from eq 10a by substituting the RRKM expression, $k(E,J) = N^{\dagger}(E,J)/h\rho(E,J)$, for all the rate coefficients, where h is Planck's constant, and $N^{\dagger}(E,J)/h$ may be regarded as a flux per unit energy through the relevant transition-state dividing surface. When this substitution is made, *all the densities of states cancel out*,[68] and we are left with the result

$$|k_0(T)\rangle = \frac{1}{hQ_{\mathrm{Rm}}(T)} \sum_J (2J+1) \int_0^\infty N_D(E,J)\, N_K^{-1}(E,J)|N_b(E,J)\rangle \mathrm{e}^{-\beta E}\, \mathrm{d}E \tag{10b}$$

where N_D, N_K^{-1}, and $|N_b\rangle$ are related to D, K^{-1}, and $|b\rangle$ in that the former contain only the numerator $N^{\dagger}(E,J)$ in the corresponding rate-coefficient expression of the latter. Of course, the components of the vector $|k_0(T)\rangle$ are the phenomenological rate coefficients for all the bimolecular product channels. The advantage of eq 10b is that one never has to evaluate the densities of states of the complexes or the reactants in using it. It can be useful and instructive to think of eq 10 as defining a matrix/integral operator that transforms the microcanonical/J-resolved association rate coefficients (fluxes) into the phenomenological, collisionless-limit rate coefficients. The reader should be able to write down by inspection the analogous operators (and equations) for the case where J is not conserved.

The other limit that is of interest is that corresponding to $Z \rightarrow \infty$, that is, the high-pressure or infinite-pressure limit. These rate coefficients can be computed simply as "capture" rate coefficients, that is,

$$|k_\infty(T)\rangle = \frac{1}{hQ_{\mathrm{Rm}}} \sum_J (2J+1) \int_0^\infty |N_b(E,J)\rangle \mathrm{e}^{-\beta E}\, \mathrm{d}E \tag{11}$$

Note that the components of $|k_\infty(T)\rangle$ and $|N_b(E,J)\rangle$ are zero unless the product of the reaction corresponds to a well that is directly connected to the reactants. Of course, one can simplify eq 11 further if one chooses to implement conventional transition-state theory in calculating the fluxes and to neglect tunneling (in which case the rate coefficients can be expressed in terms of ratios of canonical partition functions). However, we rarely choose to implement such approximations. In the present limit, that is, $Z \rightarrow \infty$, collisions are so dominant in the complexes that thermal equilibrium is established before any subsequent reaction can take place. Therefore, the only products formed are the initial adducts. A similar situation arises in isomerization. As $Z \rightarrow \infty$, only isomerization between adjacent configurations occurs. However, at lower pressures, isomerization can "skip wells". We illustrate this point below for allene isomerizing to propyne and cyclopropene.

Equation 11 has a form similar to that of eq 10b in that both can be viewed as defining operators that transform the microcanonical/J-resolved association fluxes into phenomenological rate coefficients. Alternatively, if one takes the summation over J inside the integral in the two equations, it is easy to recognize that $|k_0\rangle$ and $|k_\infty\rangle$ are both Laplace transforms of functions of the various fluxes involved in the problem, with β being the Laplace transform variable. Note that, because of the nature of the two limiting conditions, both $|k_0\rangle$ and $|k_\infty\rangle$ are flux coefficients. The steady-state approximation is universally applicable in the collisionless limit, because the lifetime of the complex is necessarily much smaller than the time between the formation of complexes under such conditions. In both limits, thermal equilibrium exists in both the reactants and products, and energy-transferring collisions play no role in determining the rate coefficients. *The general rule is that the phenomenological rate coefficient and the instantaneous flux coefficient, which remains constant in time, are identical if the reactants and all the products can be assumed to be in complete thermal equilibrium. Under such conditions, the forward and reverse rate coefficients can be treated independently and approximated as flux coefficients*. This point is discussed again below. Note that in this context "complete thermal equilibrium" refers to all energy levels, not just the low-lying ones that determine the temperature.

The General Case. As noted above, in general, it is necessary to probe the time evolution of the system under consideration to determine phenomenological or thermal rate coefficients. However, there are two special cases for which this approach is not necessary: a direct abstraction reaction and any simple association/dissociation or isomerization reaction that is occurring in its high-pressure limit. In both of these cases, one can safely assume that both the reactants and products are in thermal equilibrium. In such cases, the phenomenological rate coefficient is equal to the "equilibrium rate coefficient", k_{eq}, another rate parameter discussed by Widom. The equilibrium rate coefficient is a flux coefficient and is the long-time limit of the instantaneous flux coefficient (Widom's "r") for any two-configuration elementary reaction. Of course, in general, the latter is time dependent.

Now, let us describe how we go about solving the one-dimensional master equation and obtaining phenomenological rate coefficients from properties of its solution. First, let us consider a slightly more general approach than the one we actually use. To this end, assume that we have added terms to the ME, analogous to the $K_{\mathrm{eq}_i}k_{\mathrm{d}_i}F_i(E)n_{\mathrm{R}}n_{\mathrm{m}}$ term on the right-hand side of eq 3c, that describe reassociation of the bimolecular products. Furthermore, let us assume that for each set of bimolecular products one of the components is maintained in great excess, analogous to n_{m} for the reactants. Of course, we must add an equation similar to eq 5 for the deficient component in each of these sets of products. These assumptions maintain the linearity of the master equation and allow us to treat all the chemical configurations (wells, bimolecular products, and bimolecular reactants) equally in the analysis. We could relatively easily work with the expanded master equation just described, but instead, we assume in practice that any set of bimolecular products represents an "infinite sink", that is, that such products, once they are formed, never return to the wells. We describe this approximation after we deal with the more general case.

Equations 3c, 5, and an equation analogous to eq 5 for the "deficient reactant" in each set of bimolecular products can be combined into one (vector) master equation. After representing the integrals in these equations as discrete sums using a simple rectangle rule with grid spacing δE, one can cast the ME into the form[58]

$$\frac{\mathrm{d}|w(t)\rangle}{\mathrm{d}t} = G|w(t)\rangle \tag{12}$$

where G is a real, symmetric (and consequently Hermitian) matrix, and $|w(t)\rangle$ is a vector containing the (scaled) unknown populations

$$|w(t)\rangle = \Bigg[y_I(E_{0_I}), \ldots, y_I(E_l), \ldots, y_i(E_{0_i}), \ldots, y_i(E_l), \ldots, \left(\frac{n_{\mathrm{m}}}{Q_{\mathrm{Rm}}\delta E}\right)^{1/2} X_{\mathrm{R}}, \ldots\Bigg]^T \tag{13}$$

In this last equation, $y_i(E,t) = x_i(E,t)/f_i(E)$, where $f_i^2(E) = F_i(E)\,Q_i(T)$, $x_i(E,t)\delta E$ is the fraction of the initial reactant concentration that is present in well i with an energy between E and $E + \delta E$ at time t, and X_{R} is the fraction that is present as R at time t. Note that the term "reactant" here can refer to R, one of the other bimolecular configurations, or one of the wells. The three dots at the end indicate that there is a component of the vector of the same form as $(n_{\mathrm{m}}/Q_{\mathrm{Rm}}\delta E)^{1/2}X_{\mathrm{R}}$ for each set of bimolecular products.

The Hermiticity of the transition matrix G allows us to solve eq 12 in exactly the same way that one obtains the general solution of the time-dependent Schrodinger equation. One first solves for the eigenvalues and an orthonormal set of eigenvectors of G

$$G|g_j\rangle = \lambda_j|g_j\rangle \tag{14}$$

Expanding $|w(t)\rangle$ in this basis, one can write the solution vector in the form

$$|w(t)\rangle = \hat{T}|w(0)\rangle \tag{15}$$

where $|w(0)\rangle$ is the initial-conditions vector and $\hat{T}$ is the time evolution operator

$$\hat{T} = \sum_{j=0}^{N-1} \mathrm{e}^{\lambda_j t}|g_j\rangle\langle g_j| \tag{16}$$

In eq 16, N is the number of eigenpairs, $N = \sum_{i=I}^{M} N_i + N_p + 1$, and N_i is the number of grid points in well i; the 1 is for the bimolecular reactants.

The eigenvalues of G are always real (because G is Hermitian) and nonpositive (either zero or negative). In the present formulation, there is exactly one zero eigenvalue, $\lambda_0 = 0$, whose corresponding eigenvector yields the relative state populations at complete thermal and chemical equilibrium. The remainder of the eigenvalues must be negative

$$\lambda_j < 0, j = 1, \ldots, N - 1 \tag{17}$$

or the solution to the ME (eqs 15 and 16) would blow up as $t \to \infty$. We refer to the second largest (the least negative) eigenvalue of G as λ_1, the third largest as λ_2, and so on; the corresponding eigenvectors are $|g_1\rangle$, $|g_2\rangle$, and so forth. Once one has the solution vector, it is a straightforward matter to obtain the species concentrations (or macroscopic populations) either directly (for the bimolecular components) or from the integral

$$X_i(t) = \int_{E_{0_i}}^{\infty} x_i(E,t)\,\mathrm{d}E \tag{18}$$

for the wells. Ultimately, it is these species concentrations that interest us, not the individual energy-level populations.

Widom[27,69,70] describes the eigenpairs of G, λ_i,$|g_i\rangle$, as "normal modes of relaxation" of the system, eigenmodes. They describe the system's approach to complete thermal and chemical equilibrium from an arbitrary initial condition. N, as defined above, is almost always a number in the thousands. However, the vast majority of these modes do not describe chemical change. They simply adjust the relative populations, $x_i(E,t)$, without significantly changing the integral, $X_i(t)$. They describe the relaxation of the internal (rotational−vibrational) energy of the molecules whose stable structures correspond to the bottoms of the wells. We refer to these eigenmodes as IEREs (internal-energy relaxation eigenmodes, eigenpairs, or eigenvalues). The remainder are CSEs (chemically significant eigenvalues, eigenpairs, or eigenmodes). Under conditions where a phenomenological description of the chemical kinetics might normally be expected to apply (i.e., a description in terms of elementary reactions and rate coefficients), the IEREs relax orders of magnitude more rapidly than do the CSEs. This is enormously useful in simplifying the task of obtaining thermal rate coefficients from the eigenvalues and eigenvectors of G. In fact, one might argue that such a separation of time scales is essential for a useful phenomenological description of the chemical kinetics to apply.

If there are S species, or chemical configurations, in a problem, there are

$$N_{\mathrm{chem}} = S - 1 \tag{19}$$

chemically significant eigenmodes in addition to λ_0, $|g_0\rangle$. It is very important to understand why N_{chem} is equal to $S - 1$ and what the function is of each of these eigenmodes. Let us answer the first question first. Although we do not know the rate coefficients yet, suppose that we attempt to describe the chemical kinetics of the problem with a set of rate equations. Of course, there must be S first-order rate equations (including pseudo-first-order processes), which can be expressed in matrix form as

$$\frac{\mathrm{d}|n\rangle}{\mathrm{d}t} = K_{\mathrm{r}}|n\rangle \tag{20}$$

where K_{r} is an $S \times S$ matrix made up of the thermal rate coefficients. Although K_r is not necessarily Hermitian, we can go about solving eq 20 in exactly the same way that we solved the ME itself, that is, by diagonalizing K_r and expanding $|n\rangle$ in terms of these eigenvectors. Barring special circumstances, K_r will have S eigenvalues and S linearly independent eigenvectors, and the solution will be expressible as a linear combination of exponential functions of the form $e^{\eta_j t}$, where η_j is an eigenvalue of K_r. There must be an $\eta_0 = 0$ in order to force the concentrations to approach constant, nonzero (equilibrium) values as $t \rightarrow \infty$. The remaining $S - 1$ eigenmodes of K_r are macroscopically equivalent to the $S - 1$ CSEs of the master equation. It is this macroscopic equivalence that allows us to relate the rate coefficients to the eigenvalues and eigenvectors of G. In fact, we can infer that $\lambda_j = \eta_j$, which of course must be rigorously true, since both solutions are unique for a given set of initial conditions and describe the same physical processes.

Now let us answer the second question posed above. The establishment of chemical equilibrium occurs in well-defined stages. Each of the chemically significant eigenmodes describes the approach to chemical equilibrium of one species with one or more other species (although other chemical change can occur simultaneously). To understand this point, it is helpful to consider a simple, but nontrivial example. Suppose that $S = 4$, and let us call the four species S_1, S_2, S_3, and S_4. One way of approaching equilibrium is for the fastest-relaxing CSE to equilibrate S_1 with S_2. Then, $\lambda_2,|g_2\rangle$ could equilibrate S_3 with the S_1,S_2 pair, and the slowest-relaxing mode could equilibrate S_4 with the other three, thus establishing complete chemical equilibrium. Alternatively, $\lambda_2,|g_2\rangle$ could equilibrate S_3 with S_4, and $\lambda_1,|g_1\rangle$, the slowest-relaxing CSE, would then equilibrate the S_1,S_2 pair with the S_3,S_4 pair. Obviously, other ways of establishing equilibrium can be envisioned in the present example simply by permuting the subscripts on the S's. In more complicated problems, the number of possible ways that chemical equilibrium can be reached is quite large. Nevertheless, there are always $S - 1$ chemically significant eigenmodes.

For a problem with S species, there are N_k reversible elementary reactions occurring simultaneously, where

$$N_k = \sum_{n=1}^{S-1} n = \frac{S(S-1)}{2} \tag{21}$$

If $S = 2$, $N_k = N_{\text{chem}} = 1$, and we can obtain both the forward and reverse rate coefficients from the single eigenvalue, λ_1, and the equilibrium constant. However, in our recent study of propargyl recombination, there were 12 wells and two sets of bimolecular products, making $S = 15$, $N_{\text{chem}} = 14$, and $N_k = 105$. The actual value of N_k is almost always slightly smaller than that given by eq 21 because of our assumption that the bimolecular products constitute an infinite sink. *Nevertheless, it is this large number of elementary reactions, all occurring simultaneously, that makes it difficult to obtain the phenomenological rate coefficients directly from the time histories that come from the solution to the master equation.*

Under conditions where the IEREs relax faster than the CSEs, the macroscopic populations can be written as

$$X_i(t) = \sum_{j=0}^{N_{\text{chem}}} a_{ij} e^{\lambda_j t}, \quad i = I, ..., M, R, p_1, ... \tag{22}$$

after the IEREs relax to zero. The p_α's ($\alpha = 1, ...$) represent the different sets of bimolecular configurations other than R. The coefficient $a_{i0} = X_i(\infty)$ is the equilibrium population of the ith species, and

$$a_{ij} = -\Delta X_{ij}, \quad j \neq 0 \tag{23}$$

where ΔX_{ij} is the population change of the ith species that accompanies the time evolution of the jth eigenpair from $t = 0$ to $t = \infty$. The values of the ΔX_{ij}'s thus depend on the initial condition, but they can be readily calculated from the solution to the ME. The a_{ij}'s and the λ_j's are the fundamental quantities needed to calculate the phenomenological rate coefficients.

We have derived two different methods of obtaining the rate coefficients from the chemically significant eigenpairs. The first method, which we call the initial-rate method, utilizes different initial conditions in evaluating the a_{ij}'s in eq 22. Differentiating this equation with respect to time and taking the limit $t \rightarrow 0$ results in the rate-coefficient expressions[51]

$$\begin{aligned} k_{Ti} &= \sum_{j=1}^{N_{\text{chem}}} \lambda_j \Delta X_{ij}^{(i)} \\ k_{il} &= -\sum_{j=1}^{N_{\text{chem}}} \lambda_j \Delta X_{lj}^{(i)} \end{aligned} \tag{24}$$

where k_{Ti} is the total rate coefficient for converting species i to all products and k_{il} is the $i \rightarrow l$ rate coefficient. The superscript "(i)" on ΔX_{ij} and ΔX_{lj} indicates that species i must be the initial reactant. This method is applicable only as long as $|\lambda_{N_{\text{chem}}}| \ll |\lambda_{N_{\text{chem}}+1}|$, since "$t = 0$" must be well defined. In other words, there must exist a time period when all the IEREs have relaxed to zero, but no reaction has occurred. In general, this condition is not considered to be very restrictive. It is frequently presumed to be a necessary condition for a rate-coefficient description of the kinetics to apply.

The second approach is what we call the long-time method. It consists of recognizing that eq 22 is of the same form as the solution to eq 20, that is, the solution to a system of first-order rate equations. The task is to solve the inverse problem of finding the phenomenological rate coefficients for the system of reactions that generated the particular solution at hand. We solved this problem and obtained the following results for the rate coefficients:[51]

$$\begin{aligned} k_{Ti} &= -\sum_{j=0}^{N_{\text{chem}}} \lambda_j a_{ij} b_{ji} \\ k_{il} &= \sum_{j=0}^{N_{\text{chem}}} \lambda_j a_{lj} b_{ji} \end{aligned} \tag{25}$$

In eqs 25, if the a_{ij}'s are taken to be the elements of a matrix, A, the b_{ij}'s are the elements of its inverse, $B = A^{-1}$. Equations 25 applies to all initial conditions, and more importantly, eq 22 (and thus the rate coefficients derived from it, eqs 25) is applicable as long as $|\lambda_{N_{\text{chem}}}| < |\lambda_{N_{\text{chem}}+1}|$, a less restrictive condition than that necessary for the initial-rate method to apply. As long as the vibrational−rotational relaxation period is over before the chemistry is complete, there will be at least a short period of time, late in the course of the reaction, when a phenomenological description of the chemical kinetics will apply, with the rate coefficients given by eqs 25. It is sufficient that there exist a distinguishable period of time, however small, when eq 22 applies.

For most conditions, the initial-rate method and the long-time method give the same values for the rate coefficients. However, as the magnitude of $\lambda_{N_{\text{chem}}}$ increases and approaches that of $\lambda_{N_{\mathrm{chem}}+1}$ at high temperatures, the long-time method continues to yield good values for the rate coefficients when the initial-rate method fails. Nevertheless, the initial-rate approach is most commonly the method of choice, simply because it is easier to apply.

Blitz et al.[21] recently derived different, but equivalent, expressions for the long-time rate coefficients. They worked directly with the ME, rather than with its solution. Thus, there was no constant of integration requiring an initial condition. As a result, they were able to show explicitly that the rate coefficients obtained are independent of the initial condition.

In a seminal paper in 1974, Bartis and Widom[71] used an approach to the rate-coefficient problem similar to the long-time method described above, but with an additional assumption. The essence of this assumption is that, during the course of the reaction, the state populations are not perturbed greatly from their equilibrium values. With this assumption, Bartis and Widom derived rate-coefficient expressions analogous to eq 25 that satisfy detailed balance exactly; that is, the forward rate coefficient divided by the reverse rate coefficient equals the equilibrium constant. Although no proof exists that the rate-coefficient expressions given above satisfy detailed balance, they normally do, at least to within numerical error. We believe that detailed balance is universally valid, although no rigorous proof exists for more than “two-configuration” problems.

The rate coefficients that one derives from eqs 24 and 25 are first-order or pseudo-first-order rate coefficients. In cases where the reactions are really bimolecular, one must divide these rate coefficients by n_{m} or its equivalent to obtain the true rate coefficients. The device introduced above to linearize the master equation, particularly that of including a species in excess for all the bimolecular products, may seem somewhat artificial at first. However, one must bear in mind that our objective is to obtain the rate coefficients, which are assumed to be transportable to other environments, not to simulate the time evolution corresponding to any particular experimental condition.

In practice, we do not use the above methods exactly. Instead, we approximate all but one set of bimolecular fragments, the reactants R and m, as infinite sinks.[51] How does this change the procedures discussed above? Not very much it turns out. With the infinite-sink approximation, two differences appear in the above analysis: the system does not approach chemical equilibrium at long times, and one cannot compute ΔX_{ij} for the sinks explicitly from the solution to the ME. However, one can still obtain these quantities in a relatively straightforward manner. Assume that there is only one set of bimolecular products. The macroscopic populations satisfy the global conservation equation

$$X_{\mathrm{R}} + X_p + \sum_{i=I}^{M} X_i = 1 \tag{26}$$

Differentiating this equation with respect to time and then integrating from $t = 0$ to $t = \infty$, one obtains

$$\Delta X_{\mathrm{R}} + \Delta X_p + \sum_{i=I}^{M} \Delta X_i = 0 \tag{27}$$

Because the terms in eqs 16 and 22 are linearly independent functions of time, at least as long as no two eigenvalues are equal, eq 27 must be satisfied by each eigenpair individually, not just globally, that is,

$$(\Delta X_{\mathrm{R}} + \Delta X_p + \sum_{i=I}^{M} \Delta X_i)_j = 0 \tag{28}$$

Thus, after obtaining $\Delta X_{\mathrm{R}j}$ and ΔX_{ij} from the solution to the ME, one can calculate ΔX_{pj} from eq 28. These results, coupled with the obvious long-time limits,

$$X_p(\infty) = 1$$

and

$$X_{\mathrm{R}}(\infty) = X_i(\infty) = 0, \quad i = I, \ldots, M \tag{29}$$

can be inserted into eqs 24 and 25 to obtain the thermal rate coefficients.

It is just slightly more difficult to obtain the ΔX’s for the bimolecular products and the $t \rightarrow \infty$ population limits when there is more than one set of such products. We shall not discuss this case here. The derivation is given in detail in our paper on reactions that occur on a C_3H_4 potential.[50]

It happens frequently in practical applications that at high temperatures the large separation between the magnitudes of the CSEs and those of the IEREs ceases to exist. What happens is that a CSE increases in magnitude with temperature until it approaches the quasi-continuum of IEREs and then becomes indistinguishable from them. We can still determine rate coefficients under such conditions. One must first identify the function of the particular eigenpair that is being absorbed by the IEREs, and then at higher temperatures we combine the two (or more) species being equilibrated into one compound species. One then can proceed as described above with the values of S and N_{chem} reduced by 1. The conditions of applicability of the two methods of determining the rate coefficients must then be reinterpreted in terms of the reduced set of species. The modification to the procedure required for the initial-rate method is trivial; the number of terms in the sum is reduced by 1 (reinterpretation of the ΔX’s for the compound species is also required in principle). The modification to the long-time method, in general, requires a reformulation of the problem. This makes it more difficult to implement, making the initial-rate method the method of choice for most problems at high T.

By the phrase “a reformulation of the problem” in the last paragraph, we mean that, in the long-time method, one must examine the solution, reconstruct the A and B matrices defined above, and recalculate the rate coefficients from eq 25. This involves considerably more effort than is required for the initial-rate method and is difficult to automate in a computer calculation. In the cases where we have gone to the trouble of doing this reformulation for the long-time method, the two approaches yield the same rate coefficients. Of course, for problems with a large number of wells, and consequently a large number of CSEs, one could conceivably encounter a situation where, for a given pressure, it was not possible to find a temperature where the initial-rate method was applicable. In such situations, it would be necessary to use the more robust long-time approach. However, we have not yet encountered such a situation.

At low temperatures, it can be difficult numerically to obtain accurate eigenvalues and eigenvectors of G.[53,72,94] This problem can be overcome in either of two ways:

(1) By doing the diagonalization in quadruple-precision arithmetic, rather than double precision.[72,94] This approach is limited to relatively small problems.

(2) By integrating the ME directly in time[53] using an ODE solver, resorting to the "exponential decay" approach[51,53] to determine rate coefficients and product distributions. This approach is generally adequate at sufficiently low temperatures, where the CSEs are well separated in magnitude and "interference effects" such as those described in ref 51 can be avoided. We have used both of these methods successfully at various times.

Before going on to consider some examples it is useful to review the relationship between a rate coefficient and a flux coefficient. In doing so, we draw heavily upon Widom's discussion. Consider a first-order (or pseudo-first-order) reaction, $A \rightleftarrows B$ involving only the two configurations A and B. The net rate of formation of B (i.e., the net flux from A to B) can be written as

$$\frac{dn_B}{dt} = -\frac{dn_A}{dt} = k_f n_A - k_r n_B \tag{30}$$

The question is "What are k_f and k_r?" One is instinctively tempted to identify $k_f n_A$ and $k_r n_B$ as the individual forward and reverse fluxes, respectively. In which case, k_f and k_r are the probabilities per unit time of an $A \rightarrow B$ and $B \rightarrow A$ transition; that is, they are flux coefficients. The problem with this identification is that in general k_f and k_r are both time dependent, and they do not satisfy detailed balance. The true rate coefficients satisfy eq 30, are not time dependent, and do satisfy detailed balance. However, with the true rate coefficients inserted into eq 30, the two terms on the right-hand side cannot be interpreted as the individual forward and reverse fluxes. That is the central issue. However, for many cases, the instantaneous flux coefficients and the rate coefficients are virtually indistinguishable. For simple abstraction reactions and high-pressure-limit, unimolecular isomerization or dissociation reactions, they are identical, because thermal equilibrium is suitably maintained, or assumed to be maintained, throughout the course of the reaction. The equivalence of the two rate parameters in these special cases is probably the origin of the confusion that exists on this issue. The situation for nonequilibrium problems is counterintuitive even in the two-configuration case; one must expect it to be even more so for an arbitrary number of configurations.

In many circumstances, we write the rate law simply as

$$-\frac{dn_A}{dt} = k_f n_A \tag{31}$$

We might write it this way, as in the theoretical analysis of thermal dissociation, because we believe the reverse process has no effect on the rate coefficient, or it can be that the second term in eq 30 is negligible. In calculating the equilibrium rate coefficients mentioned just above, the fluxes in the two directions are independent and can be calculated separately. Thus, we are always dealing with a rate law in the form of eq 31. In all such cases where eq 31 applies, the net flux and the forward flux are identical, making the flux coefficient and the rate coefficient the same parameter. Of course, the negligibility of the second term in eq 30 is the idea behind the exponential decay approach to measuring the rate coefficients at low temperatures. Equation 30 also gives an exponential decay for the reactant, but the decay is not to zero, and the decay constant is not simply the rate coefficient.

Examples

The Reaction between Ethyl and Molecular Oxygen. A particularly simple and instructive example of the power of the methods described above is the reaction of C_2H_5 with O_2. The PES is depicted diagrammatically in Figure 1. We shall be concerned here only with the bimolecular channel leading to $C_2H_4 + HO_2$ (and only the initial $C_2H_5O_2$ adduct); it is overwhelmingly dominant under the conditions of interest anyway. The bimolecular products are incorporated into the analysis as an infinite sink. Thus, we have $S = 3$, $N_{chem} = 2$, and $N_k = 3$. For future reference, the eigenvalue spectrum of G is plotted in Figure 2 for a pressure of 1 atm; the equilibration functions of the CSEs are shown on the diagram.

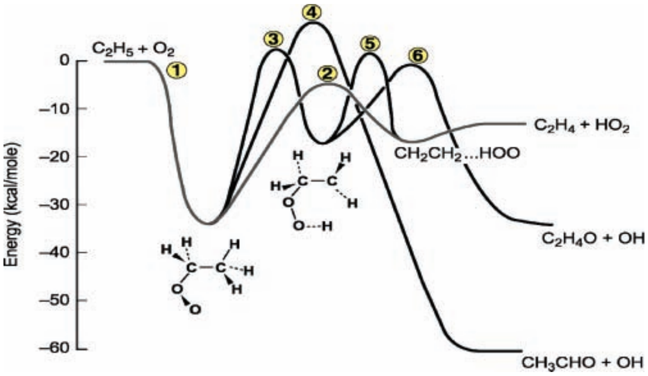

Figure 1. Potential energy diagram for the $C_2H_5 + O_2$ reaction.

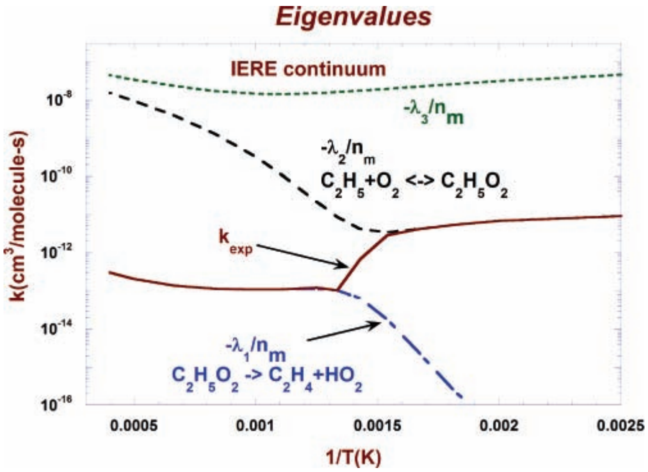

Figure 2. Eigenvalue spectrum for $C_2H_5 + O_2$ at $p = 1$ atm. The eigenvalues are divided by n_m to show their relationship to the decay constant.

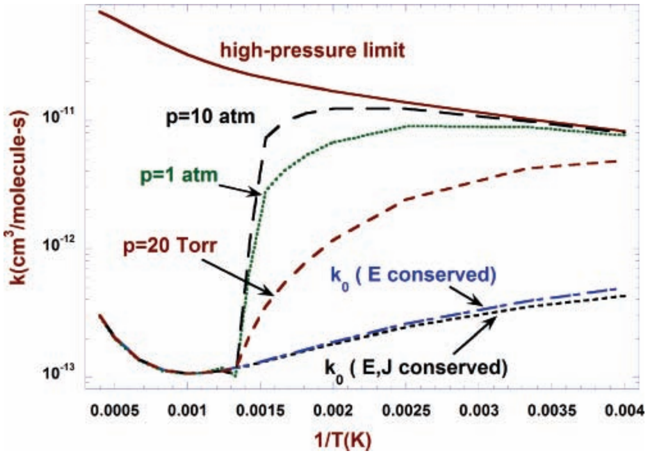

Figure 3. Decay constants as a function of temperature at various pressures for $C_2H_5 + O_2$.

Figure 3 displays the limiting rate coefficients $k_0(T)$ and $k_\infty(T)$ and "rate coefficients", k_{exp}, derived from the exponential decay of R, the reactant, at three different pressures (20 Torr, 1 atm, 10 atm). Both the 1-D and 2-D values for $k_0(T)$ are shown on the plot. At 250 K, the smallest temperature shown, the 1-D solution for $k_0(T)$ is about 15% larger than the 2-D solution; the difference gradually becomes even smaller as the temperature increases. Although in general such differences depend on a number of factors, most notably the potential energy difference between TS-1 and TS-2 (transition states 1 and 2, respectively) and the corresponding rotational constants, the present result is fairly typical. Consequently, angular momentum conservation is usually not an important factor for bimolecular reactions producing bimolecular products.

The exponential decay rate coefficients shown in Figure 3 display some intriguing features. At temperatures up to $T \approx 575$ K, one obtains excellent exponential decays, and the distribution of products accumulated at the end of the decay period depends on both temperature and pressure. The bimolecular products $C_2H_4 + HO_2$ are dominant at lower pressures, and the stabilized adduct $C_2H_5O_2$ becomes more and more prevalent as the pressure is increased. Of course, this is the expected behavior. In the temperature range roughly between 575 and 700 K, the good exponential decays disappear. Instead, the reactant decay becomes biexponential. Then, again for $T > 700$ K, nearly perfect exponential decays of the reactant return. However, now the rate coefficient becomes equal to $k_0(T)$, and the only products are $C_2H_4 + HO_2$, *independent of temperature and pressure.*

The behavior at high temperature described in the previous paragraph is remarkable. Some comments are in order. The exponential decay approach to obtaining rate coefficients is equivalent to computing a flux coefficient from a steady-state energy distribution in the well. The discussion centered around eq 31 indicates clearly that such coefficients can indeed be interpreted as (constant) probabilities per unit time of making the indicated transformations. At least for the case of the $C_2H_4 + HO_2$ products, this is not exactly what Widom had in mind for his flux coefficients, but his discussion does not anticipate the necessity of passing through two transition states to get from reactants to products. The important question is "Have we really determined rate coefficients?"

A critical point to bear in mind in answering this question is that *exponential decay of the reactant indicates that the reaction is controlled by a single chemically significant eigenmode of G, not by a single elementary reaction* (single-channel or multiple-channel). At low temperatures, the two generally coincide very closely, that is, eigenmode ≈ multichannel elementary reaction, at least partly because the CSEs are widely separated in magnitude. However, this is not always the case, particularly at high T. Referring to Figure 2, one can see that $\lambda_2,|g_2\rangle$ describes the equilibration of $C_2H_5 + O_2$ with $C_2H_5O_2$ ($C_2H_4 + HO_2$ can also be formed as a product). At low temperatures, the reactant concentration decays exponentially to zero, because the equilibrium constant is so large, at a rate determined exclusively by λ_2. The $\lambda_1,|g_1\rangle$ eigenpair describes the "equilibration" of $C_2H_5 + O_2$ and $C_2H_5O_2$ with the $C_2H_4 + HO_2$ infinite sink. At low temperatures, this eigenmode can be very closely identified with the thermal dissociation of $C_2H_5O_2$ to form $C_2H_4 + HO_2$, again because the $C_2H_5 + O_2 \rightleftarrows C_2H_5O_2$ so heavily favors the adduct under such conditions.

From Figure 2, one can see that λ_1 and λ_2 approach each other in the 575 K < T < 700 K range (they approach more closely as the pressure is reduced[55]), undergoing what might be called an avoided crossing. In this region, what we have previously called the transition regime,[55,56] both eigenmodes contribute to the decay of R, the reactant, and hence, we get biexponential decays. When the two CSEs emerge from the transition regime at high T, some important changes have occurred. The $\lambda_2,|g_2\rangle$ eigenpair still describes the equilibration $C_2H_5 + O_2 \rightleftarrows C_2H_5O_2$, but now this equilibrium heavily favors $C_2H_5 + O_2$; that is, the equilibrium has shifted. Also, λ_1 and $|g_1\rangle$ still describe the equilibration of $C_2H_5 + O_2$ and $C_2H_5O_2$ with $C_2H_4 + HO_2$, but because the equilibrium mixture of $C_2H_5 + O_2$ and $C_2H_5O_2$ is virtually all the former, this eigenmode results in nearly perfect exponential decays of the reactant. The reason the apparent rate coefficients deduced from the reactant decays in this high-temperature region are all equal to $k_0(T)$, independent of pressure, is discussed in detail in ref 55. We shall not repeat that discussion here.

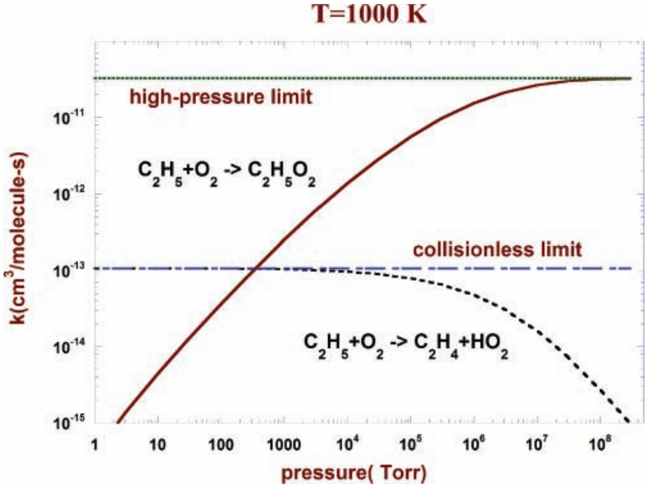

Figure 4. Rate coefficients as a function of pressure at $T = 1000$ K for $C_2H_5 + O_2 \rightarrow C_2H_5O_2$ and $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$.

Are the flux coefficients that are deduced from the exponential decays in the high-temperature regime rate coefficients, or are they not? It should be clear now that the answer to this question is that they are not. The observed behavior is a consequence of two processes (both of which can occur simultaneously): the elementary reaction $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ and the two-step process, $C_2H_5 + O_2 \rightleftarrows C_2H_5O_2$ followed by $C_2H_5O_2 \rightarrow C_2H_4 + HO_2$, both of whose rates are controlled by the same transition state, TS-2 of Figure 1. (An elementary reaction is a chemical process whose rate can be characterized by a single phenomenological rate coefficient, $k(T,p)$, under all thermally equilibrated conditions, that is, where T can be defined.) The elementary reaction is dominant at low pressure, and the two-step sequence is dominant at high pressure. The steady-state energy distribution in the well varies from a chemically activated one at low pressure to a completely thermally equilibrated one at high pressure, just as at low temperature. Remarkably, simply observing the decay of the reactant concentration and the rise of the products is insufficient to distinguish one mechanism from the other. However, the methodology described above for determining the rate coefficients can make the distinction.

In Figure 4, we plot the rate coefficients for the two reactions, $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ and $C_2H_5 + O_2 \rightarrow C_2H_5O_2$, as a function of pressure for a temperature of 1000 K. A relatively small fraction of the $C_2H_5O_2$ formed from the stabilization reaction dissociates thermally to form $C_2H_4 + HO_2$; most of it just dissociates back to $C_2H_5 + O_2$. For the stabilization reaction, the only one for which we can calculate forward and reverse rate coefficients, detailed balance is satisfied to the numerical accuracy of the calculation.

Allene−Propyne Isomerization. Perhaps the most counterintuitive phenomenon associated with the multiple-well master

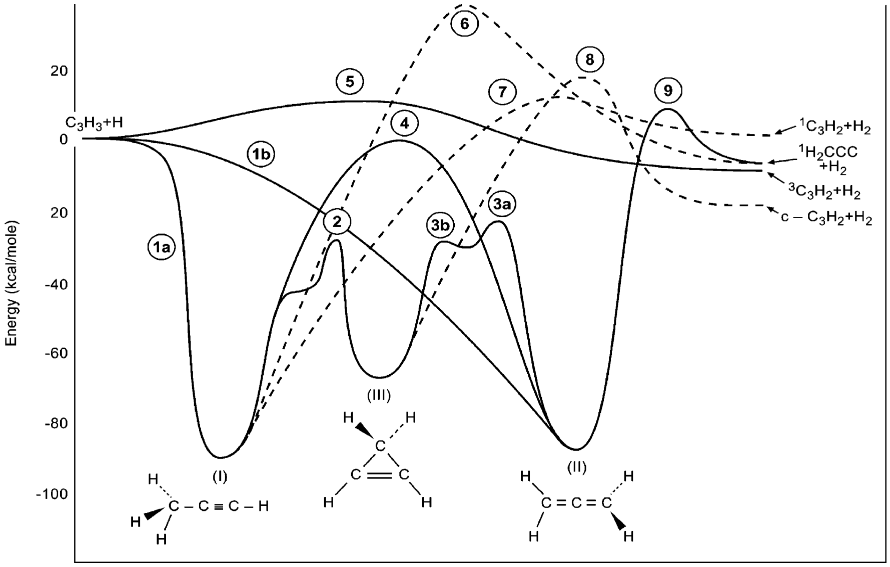

Figure 5. Potential energy diagram for the C_3H_4 surface.

equation is an *isomerization reaction that skips one or more wells*. Although in principle such a reaction is no different from an association/dissociation reaction that skips a well, the isomerization is more unexpected to the average chemical kineticist. Such reactions are the best illustrations we have of the difference between the rate coefficients, or transition probabilities, that appear in the master equation and the rate coefficients that appear in macroscopic rate laws. The former are course-grained, statistical substitutes for dynamics, and consequently, they connect only adjacent configurations. The latter are purely phenomenological and are not bound by such a constraint.

As an illustration of an isomerization reaction that skips a well, consider the isomerization of allene[50] (C_3H_4a). The potential on which we base our analysis is illustrated in Figure 5. The diagram shows a number of configurations on the singlet potential and indicates the possibility of a hydrogen abstraction reaction, $C_3H_3 + H \rightarrow {}^3C_3H_2 + H_2$, where ${}^3C_3H_2$ is triplet propargylene, on a triplet potential. This latter reaction will not concern us further in this article. On the singlet PES, there are seven distinct molecular configurations, $S = 7$. However, because we lump all three sets of bimolecular products (${}^1C_3H_2 + H_2$, ${}^1H_2CCC + H_2$, and c-$C_3H_2 + H_2$) into an infinite sink, our master equation recognizes only $S = 5$, and consequently, $N_{chem} = 4$. If we were to take $S = 7$, there would be $N_k = 21$ forward elementary reactions going on simultaneously. However, because of the infinite-sink approximation, $N_k = 18$. The three reactions that are missing are ones that have sink species both as reactants and products. Moreover, any reaction that has a sink configuration as a product has its reverse reaction missing.

The eigenvalue spectrum at $p = 1$ atm for the problem at hand is shown in Figure 6. The equilibration functions of the chemically significant eigenmodes are given on the plot. At low temperatures, the fastest-relaxing CSE equilibrates $C_3H_3 + H$ (R) with C_3H_4p (I). The second fastest equilibrates R and I with cyclopropene (III). The third fastest equilibrates these three configurations with allene (II), and the slowest of the CSEs "equilibrates" R, I, II, and III with the bimolecular sink. Because we have labeled the eigenvalues in the diagram by their functions, not by their magnitudes, there is some magnitude switching at high *T*. Nevertheless, the diagram is labeled clearly and correctly.

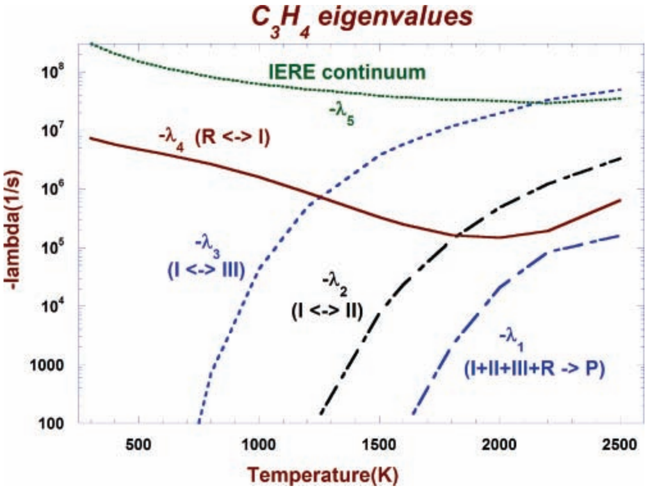

Figure 6. Eigenvalue spectrum for the C_3H_4 potential energy surface. The eigenvalues in the diagram are labeled by their function. In a similar diagram in ref 50, we simply labeled the eigenvalues by their magnitude.

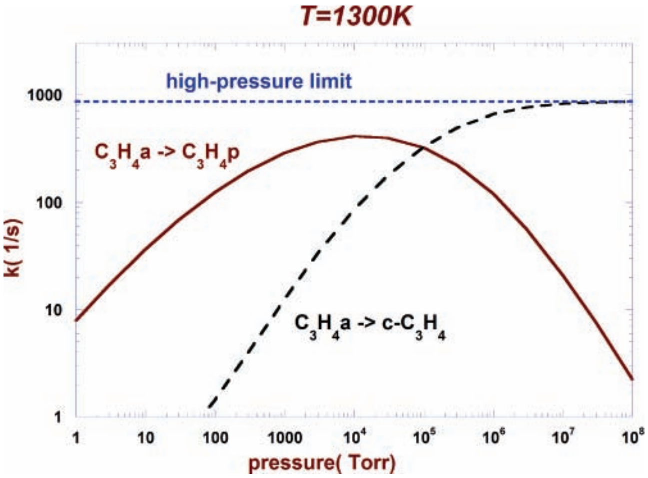

Figure 7. Rate coefficients for $C_3H_4a \rightarrow C_3H_4p$ and $C_3H_4a \rightarrow$ c-C_3H_4 as a function of pressure at $T = 1300$ K.

That brings us to the $C_3H_4a \rightleftarrows C_3H_4p$ isomerization. The rate coefficients for both $C_3H_4a \rightarrow C_3H_4p$ and $C_3H_4a \rightarrow$ c-C_3H_4 are shown in Figure 7 as a function of pressure at a temperature of 1300 K. Before going any further, it is important to point out that TS-4 in Figure 5 is inconsequential to the analysis. We could increase its energy to arbitrarily large values without changing the results of Figure 7. All the propyne formed in the reaction goes through the c-C_3H_4 well. At low pressures, the c-C_3H_4* complexes do not suffer enough collisions for any significant amount of stabilization to occur. Because of the deeper well, C_3H_4p* complexes live longer, and stabilization in this well dominates the reaction. As the pressure increases up to about 10^4 Torr, both rate coefficients increase, a consequence of increasing thermal excitation of the allene. Of course, this is the same phenomenon as the one that occurs in thermal dissociation. Beyond this pressure, the C_3H_4a → C_3H_4p rate coefficient drops off with increasing p, whereas that for C_3H_4 → c-C_3H_4 continues to rise. The latter reaction increasingly robs flux from the former. As discussed above, at infinite pressure, the rate coefficient approaches $k_\infty(T)$, and the only product corresponds to an adjacent configuration, cyclopropene in this case. Of course, one should realize that the C_3H_4a → c-C_3H_4 reaction would be totally invisible in a normal kinetics experiment, because equilibrium overwhelmingly favors the reactant, with c-C_3H_4 thermally isomerizing back to allene as fast as it is formed.

It is tempting to try to analyze the present reaction using methods similar to those used for thermal dissociation. One could apply the steady-state approximation to the allene well and then calculate the flux coefficient for passage through TS-3 ($N_3^\dagger = N_{3a}^\dagger N_{3b}^\dagger/(N_{3a}^\dagger + N_{3b}^\dagger)$ in our analysis[50]). The only objective approximation one could make about this flux is that it all leads to c-C_3H_4, which of course is wrong. One might then try to make assumptions concerning complex lifetimes (c-C_3H_4* and C_3H_4p*) and collision rates, e.g., the strong-collider or modified strong-collider assumption. However, such assumptions are unreliable and too arbitrary to form a basis for a fundamental theory of reaction rates.

The C_3H_4 potential contains a wealth of interesting illustrations of the multiple-well ME methodology. From Figure 6, one can see (for $p = 1$ atm) that at $T \approx 2150$ K λ_3 merges with the continuum of IEREs, indicating that the c-C_3H_4 ⇄ C_3H_4p isomerization equilibrates on internal-energy relaxation time scales. Thus, for kinetics purposes, c-C_3H_4 and C_3H_4p cease to be independent species and must be combined into one compound species (dominated by propyne) at higher temperatures. Also, for temperatures greater than about 1800 K, allene equilibrates with propyne (and thus also with cyclopropene) faster than dissociation to C_3H_3 + H can occur, $-\lambda_2 < -\lambda_4$. At $T = 2200$ K, $\lambda_2/\lambda_4 \approx 6$. At such temperatures (where dissociation rate coefficients might be measurable), determining the individual dissociation rate coefficients becomes problematic; most experiments will be sensitive only to λ_4, which describes the dissociation of the three equilibrated isomers. In fact, before reading this article, one might be tempted to look at Figure 5 (where all the isomerization barriers lie well below the dissociation limit) and question whether individual dissociation rate coefficients for the isomers even exist. Of course, they do exist. Our calculations indicate that allene dissociates 10−20% faster than propyne for 1800 K < T < 2500 K, whereas the experiments of Kiefer et al.[73] indicate the reverse. Either could be correct; the difference is well within the uncertainties of the theory and the experiment.

Thermal Dissociation and Association

Virtually all of our understanding of nonequilibrium phenomena in chemical kinetics comes from analyzing two-configuration problems, specifically the *irreversible* dissociation of a molecule or radical (which actually involves only one configuration) and the two-well isomerization reaction.[74−77] From the first of these, one finds that, during the steady-state dissociation process, population of bound states near the dissociation limit below their equilibrium values can reduce the dissociation rate coefficient (in the low-pressure limit) by as much as 2 orders of magnitude.[78] The two-well isomerization is primarily responsible for our realization that rate coefficients are functions of all the transition probabilities in the system, not just those of the reactant.[27] Quack[74] and Lin and Laidler[75] showed that, for specific reactions, the forward rate coefficient at low pressures can be controlled primarily by deactivation of highly excited states of the *product*. Of course, both of these phenomena can be derived as special cases of the multiple-well formalism described above. Nevertheless, we want to consider the thermal dissociation problem in more detail. This interest stems from our concern with *weakly bound free radicals*, which we define as free radicals that dissociate primarily to a *stable molecule and a radical* (rather than two free radicals). The bond energies for such dissociations are generally small, and consequently, such radicals dissociate rapidly in flames, fast enough that thermal dissociation is their primary fate under many conditions. Examples of such radicals include vinyl, ethyl, vinoxy, acetyl, i-C_4H_3, n-C_4H_3, i-C_4H_5, n-C_4H_5, allyl, and other C_3H_5 isomers. Therefore, we want to understand as much as possible about these simple reactions.

The remainder of this article is concerned with two issues: (1) an approximate solution to the two-dimensional, single-well, multiple-channel master equation for thermal dissociation and (2) an evaluation of when and if the dissociation rate coefficients derived from an irreversible ME (i.e., the unidirectional flux coefficients) represent accurate rate coefficients for the two-configuration problem.

We also discuss the issue of when and if the thermal dissociation and reverse association rate coefficients satisfy detailed balance. Specifically, we want to understand the limitations of calculating the dissociation rate coefficients from an irreversible master equation and determining the reverse association rate coefficient from detailed balance.

Approximate Solution to the Two-Dimensional Master Equation for Irreversible Thermal Dissociation. The two-dimensional master equation for the *irreversible* dissociation of a molecule (or radical) immersed in an inert gas can be written as

$$\frac{\mathrm{d}x(E,J,t)}{\mathrm{d}t} = Z\sum_{J'}\int_{E_0}^{\infty}[P(E,J;E',J')\,x(E',J',t) - P(E',J';E,J)\,x(E,J,t)]\mathrm{d}E' - \sum_{p=1}^{N_p}k_p(E,J)\,x(E,J,t) \quad (32)$$

where the symbols are defined above. For the simplification described below to be realized, it is important that the association terms corresponding to the reverse of the $k_p(E,J)$ terms in eq 32 be absent. Smith and Gilbert[60] were the first to realize that if the energy transfer function $P(E,J;E',J')$ could be written in the special form

$$P(E,J;E',J') = P(E,E')\,\phi(E,J) \quad (33)$$

the two-dimensional master equation, eq 32, could be reduced to an equivalent 1-D ME. Equation 33 requires that the J distribution after a collision be independent of the angular momentum of the molecule before the collision. In what we call our E,J model, we assume that $\phi(E,J)$ is given by

$$\phi(E,J) = (2J + 1)\,\rho(E,J)/\rho(E) \quad (34)$$

where

$$\rho(E) = \sum_J (2J+1)\ \rho(E,J) \tag{35}$$

The physical implication of this assumption is that rotational energy is transferred in quantities similar to those for vibrational energy and that the postcollision J distribution is simply proportional to the number of states in the vicinity of any E and J. The approximation is consistent with classical trajectory calculations in that a collision usually results in comparable quantities of rotational and vibrational energy being transferred. Moreover, values of $\langle \Delta E_d \rangle$ deduced from applying this model to thermal dissociation experiments are similar to those determined from direct experiments and from trajectory calculations.[78]

The mathematical details of reducing eq 32 to its equivalent 1-D form are given by Miller et al.[78] and Miller and Klippenstein.[48] The derivation offers no mathematical or conceptual difficulties and is omitted here. Although some subtle effects[34,79] are missing from this model, it allows us to include all the effects on unimolecular rate coefficients normally associated with molecular rotation.

Another approach to the problem at hand is to take ϵ and J as the independent variables in the master equation, rather than E and J, where ϵ is the energy in the "active" degrees of freedom

$$\epsilon = E - BJ(J+1) \tag{36}$$

and B is the appropriate rotational constant. This is the approach taken by Smith and Gilbert.[60] It is equivalent to partitioning the total energy into two types, whereas the E,J model is not. The master equation in this approach is identical in form to eq 32, with ϵ replacing E. Smith and Gilbert reduced the two-dimensional ME to an equivalent 1-D form by making a "strong-collisions-in-J" approximation (the ϵ,J model), whereby

$$P(\epsilon,J;\epsilon',J') = P(\epsilon,\epsilon')\ \Phi(\epsilon,J) \tag{37}$$

and

$$\Phi(\epsilon,J) = (2J+1)\ \rho(\epsilon,J)\mathrm{e}^{-\beta E_J} / \sum_J (2J+1)\ \rho(\epsilon,J)\mathrm{e}^{-\beta E_J} \tag{38}$$

In eq 38, $E_J = BJ(J+1)$ and $\rho(\epsilon,J)$ is the density of states of the *inactive* (rotational) degrees of freedom with angular momentum quantum number J (this formulation is actually slightly more general than the one used by Smith and Gilbert). This model forces complete "rotational" equilibrium to be re-established after every collision.

In studying the dissociation of methane in the low-pressure limit,[78] we used the ϵ,J model, the E,J model, and the E model (the one-dimensional ME with E being the independent variable) to analyze the best experimental results available. The E,J model and the E model produced very similar results, at least at high temperatures, indicating that the rotational degrees of freedom behave as if they are active. Unlike the E,J and E models, the ϵ,J model caused us to deduce from the experiments unrealistically small values of $\langle \Delta\epsilon_d \rangle$, as small as a few cm^{-1} under some conditions. Although we have not investigated this point in any detail, it appears likely that this effect arises from the strong-collision-in-J approximation forcing rotationally equilibrated populations on bound states near the dissociation limit, thus artificially increasing the rate coefficient. As a result, the values of $\langle \Delta\epsilon_d \rangle$ that we deduced are much too small.

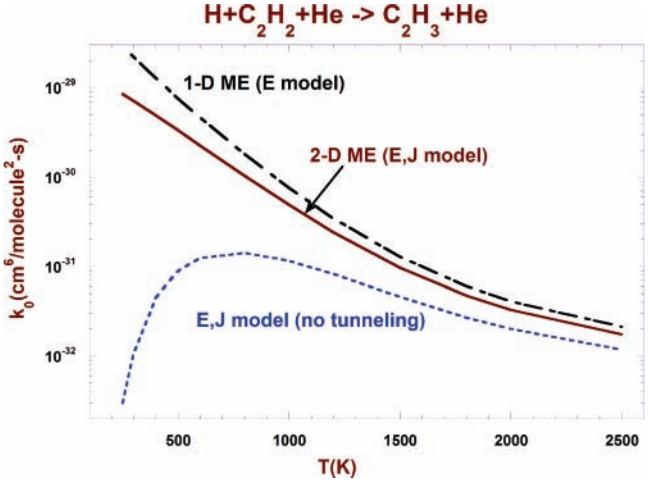

Figure 8. Low-pressure-limit rate coefficients, $k_0(T)$, for H + C_2H_2 + He → C_2H_3 + He.

In principle, one could use a variety of functions for $\phi(E,J)$ and $\Phi(\epsilon,J)$ in eqs 34 and 38 and get different results. However, the distributions assumed above appear to be the only ones that are consistent with detailed balance in that they ensure that rotational equilibrium would be approached at long times in the analogous reversible, two-configuration problem.

In Figure 8, we explore the effects of angular momentum conservation (and tunneling) on the dissociation of vinyl, a good example of a weakly bound free radical. These effects manifest themselves most visibly at the low-pressure limit. Consequently, we focus our attention on the low-pressure-limit rate coefficient, $k_0(T)$ (not to be confused with the collisionless-limit rate coefficient discussed above), for the association reaction, H + C_2H_2 + He → C_2H_3 + He, plotted in Figure 8. The association rate coefficient is obtained from the dissociation rate coefficient, calculated using the E,J and E models just described, and the equilibrium constant using the detailed balance condition. The validity of this approach is discussed below. Figure 8 shows that angular momentum conservation reduces the rate coefficient by a factor of 3.5 at 250 K. This difference becomes smaller as the temperature is increased up to 2500 K, but it never quite disappears. The difference between the E,J and E model predictions is 21% at 2500 K. These results are fairly typical.

An even more intriguing effect on the rate coefficient is that of tunneling. The dissociation of a weakly bound free radical virtually always has an intrinsic potential energy barrier (a barrier in the exothermic direction). If one of the dissociation products is a hydrogen atom, tunneling through the barrier is an extremely important effect. Figure 8 shows that tunneling increases that rate coefficient at 250 K in the present case by almost 4 orders of magnitude; the effect decreases of course as the temperature increases. Most interestingly, the inclusion of tunneling causes k_0 always to be a decreasing function of T, no matter what the size is of the intrinsic barrier. The rate coefficient behaves as if the barrier is not there! Upon first glance, this result is surprising, but upon reflection, it is not. Viewed from the dissociation direction, the low-pressure limit is reached (by definition) when dissociation above threshold becomes infinitely fast compared to collisional excitation and de-excitation. For the present reaction, and others like it, the dissociation threshold is just the bond energy, not the bond energy plus the barrier. However, dissociation just above the threshold is extremely slow in such cases, because it occurs strictly by tunneling. Consequently, the low-pressure limit is approached very slowly by these reactions.

Reversible and Irreversible Dissociation: The Detailed Balance Condition. It is rather remarkable that it has become common practice in chemical kinetics to approximate a dissociation rate coefficient as the flux coefficient obtained from treating the dissociation *irreversibly* and then to compute the recombination (or association) rate coefficient from detailed balance. It is common to do this even when equilibrium heavily favors the recombination product. One would not think of applying such a procedure universally to the two-well isomerization problem for reasons noted above. Consequently, it appears to be worthwhile to inquire about when and if such a procedure produces accurate rate coefficients.

The question of whether, for diatomic molecules, the dissociation and reverse association rate coefficients satisfy detailed balance was discussed extensively in the 1950s and 1960s.[76,80−89] The issue arose, at least partially, from the realization of the point mentioned above, that the populations of bound states near the dissociation limit are substantially depleted below their equilibrium values during the steady-state dissociation process. There was a point of view that such states must maintain equilibrium populations for detailed balance to be satisfied. Arguments in favor of the applicability of detailed balance ultimately won out. However, these arguments were largely qualitative or semiquantitative and universally imposed the condition that $\tau_v/\tau_r \ll 1$, where τ_v is the vibrational relaxation time and τ_r is the characteristic time for reaction to occur. Important contributions to our understanding of this issue were made by Keck and Carrier[85] and particularly by Rice.[80]

In 1989, Smith et al.[90] made a pivotal contribution to our understanding of the problem at hand, not limiting their considerations to diatomic molecule dissociations. From a suitably formulated master equation, they attempted to derive the detailed balance condition

$$\frac{k_{\mathrm{add}}}{k_{\mathrm{d}}} = K_{\mathrm{eq}} \tag{39}$$

for the reversible reaction, R + m $\rightleftarrows$ C, where K_{eq} is the equilibrium constant for the association reaction. Under the same conditions as those described just above, they derived the rate equation

$$\frac{\mathrm{d}n_{\mathrm{C}}(t)}{\mathrm{d}t} = -k_{\mathrm{u}} n_{\mathrm{C}}(t) + f_{\mathrm{ne}} k_{\mathrm{u}} K_{\mathrm{eq}} n_{\mathrm{m}}(t)\, n_{\mathrm{R}}(t) \tag{40}$$

where $k_{\mathrm{u}} \equiv -\xi_1$, and ξ_1 is the largest (least negative) eigenvalue of the transition matrix G' of the ME describing *irreversible* dissociation. G' is the same as G described above except that the reverse association rates are missing. The "nonequilibrium factor", f_{ne}, is a function of the steady-state energy distribution, $c(E)$, of the dissociating molecule during its irreversible dissociation. This distribution can be obtained simply by unscaling the vector $|g_1'\rangle\langle g_1'|w(0)\rangle$, where $|g_1'\rangle$ is the eigenvector of G' corresponding to ξ_1. If $c(E)$ is suitably normalized so that $\int_{E_0}^{\infty} c(E)\,\mathrm{d}E = 1$, f_{ne} can be written as

$$f_{\mathrm{ne}} = 1/\left[\int_{E_0}^{\infty} \frac{c(E)}{F(E)} c(E)\,\mathrm{d}E\right] \tag{41}$$

From eq 41, one can see that f_{ne} is a measure of the degree to which dissociation perturbs the equilibrium distribution of the dissociating molecule, $0 \le f_{\mathrm{ne}} \le 1$.[78,90,92] If only the states that are not heavily populated at equilibrium have their populations significantly depleted by dissociation, f_{ne} is very, very close to unity. This is the normal situation for stable molecules.

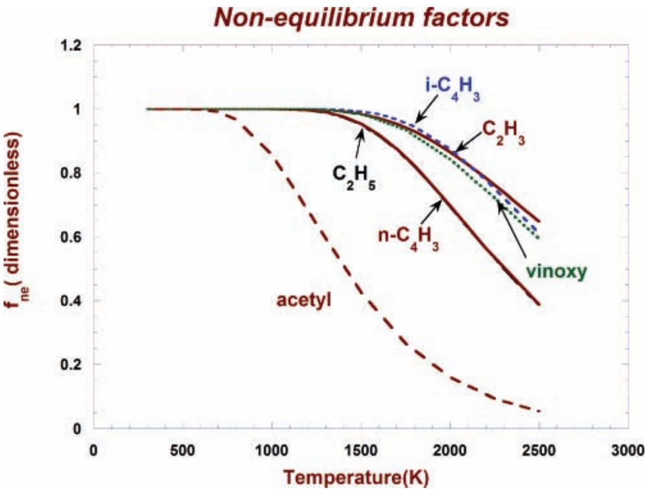

Figure 9. The nonequilibrium factor, f_{ne}, for several weakly bound free radicals at a pressure of 1 atm.

From eq 40, one can readily make the identification that $k_{\mathrm{d}} = k_{\mathrm{u}}$ and $k_{\mathrm{add}} = f_{\mathrm{ne}} K_{\mathrm{eq}} k_{\mathrm{u}}$. Except for the annoying f_{ne} factor in k_{add}, these rate coefficients would satisfy detailed balance. As it is, eq 39 is satisfied only if f_{ne} is equal to unity, which is at odds with the work on diatomic molecules mentioned above. If one takes the limit of eq 40 as $t \to \infty$, one obtains the relation

$$f_{\mathrm{ne}} K_{\mathrm{eq}} = \frac{n_{\mathrm{C}}(\infty)}{n_{\mathrm{m}}(\infty)\, n_{\mathrm{R}}(\infty)} \tag{42}$$

Thus, the system described by eq 40 approaches equilibrium at long times only if $f_{\mathrm{ne}} = 1$. Clearly, this cannot be correct. Either eq 40 is not applicable at long times or it applies only if $f_{\mathrm{ne}} = 1$. One can also conclude simply from taking this limit that if the system obeys a phenomenological rate law at long times, the rate coefficients must necessarily satisfy detailed balance.

Smith et al.[90,91] indicate that f_{ne} is equal to unity in most cases and emphasize this condition. However, such is not the case for weakly bound free radicals at high temperatures, an important application for combustion. In Figure 9, we have plotted f_{ne} for a number of radicals as a function of temperature at a pressure of 1 atm. In all cases, f_{ne} deviates from unity to some extent for $T > 1000$ K. The worst cases are for large molecules with weak bonds, where the peak in the Boltzmann distribution can lie close to the dissociation threshold, or even above it. The nonequilibrium factor gets smaller as the pressure is reduced, an important consequence for low-pressure flame experiments. Of course, as $p \to \infty$, $c(E) \to F(E)$, and f_{ne} becomes identically equal to unity. One should not confuse this effect ($f_{\mathrm{ne}} < 1$) with that discussed above, i.e., the reduction of the dissociation rate coefficient in the low-pressure limit due to underpopulated bound states near the dissociation threshold. One can have substantial reduction of such rate coefficients and still have $f_{\mathrm{ne}} \approx 1$, because states near the dissociation limit are not highly populated at equilibrium in such cases.

One can begin to resolve the issue discussed above by applying the general multiple-well methodology to the reversible association/dissociation problem. We shall omit the details, but both the long-time and initial-rate methods yield rate coefficients that satisfy detailed balance, eq 39, exactly.[92] The fact that the long-time rate coefficients satisfy detailed balance indicates that, no matter how much of the reaction takes place during the vibrational−rotational relaxation period, the last stage of the reaction always satisfies a phenomenological rate law with rate coefficients that satisfy detailed balance. One might also have drawn the same conclusion simply by extending Widom's analysis of first-order reactions[27] to pseudo-first-order processes.

Smith et al. did not pose the problem as we have. They assumed the reaction to be approaching equilibrium from the association direction, $n_C(0) = 0$, and took the association rate terms to be an external source in the master equation.[90,92] In this approach, they must evaluate $n_C(t)$ from an integral, and in so doing, they assumed that all of $n_C(t)$ was produced through the slowest-relaxing eigenmode of the system, ξ_1 and $|g'_1\rangle$. It turns out that this is completely equivalent to assuming that $f_{ne} = 1$; it is also equivalent to taking the limit $\xi_1/\xi_j \rightarrow 0$, $j \geq 2$. Therefore, with $f_{ne} = 1$, for the same conditions as those described above, $\tau_v/\tau_r \ll 1$, Smith et al. established the important result that $k_d = k_u = -\xi_1$ and $k_{add} = k_d K_{eq}$. Moreover, they did it without assuming $n_m \gg n_R$, that is, without imposing pseudo-first-order conditions.

To go beyond the Smith et al. analysis, it is necessary to assume that the reaction is pseudo-first-order. One can then express the integral mentioned above as a sum of series in the small parameters, ξ_1/ξ_j, $j \geq 2$. The next higher-order terms beyond those included by Smith et al. can be evaluated exactly, and the ones beyond that can be evaluated approximately, thus allowing the series to be summed and expressed in closed form. The resulting phenomenological rate law, analogous to eq 40, is[92]

$$\frac{dn_R}{dt} = -\frac{dn_C}{dt} = \frac{k_u}{[1 + n_m K_{eq} \sum_{j=2}^{N} f_{ne}^{(j)}]} n_C - \frac{k_u K_{eq} (\sum_{j=1}^{N} f_{ne}^{(j)})}{[1 + n_m K_{eq} \sum_{j=2}^{N} f_{ne}^{(j)}]} n_m n_R \quad (43)$$

where N is the number of eigenvectors of G', and $f_{ne}^{(j)}$ for $j \geq 2$ is defined for the higher eigenvectors in exactly the same way that $f_{ne} \equiv f_{ne}^{(1)}$ is defined for $|g'_1\rangle$. Equation 43 was derived to be applicable at long times, completely analogous to the long-time rate coefficients discussed above. Therefore, it must apply as the system approaches equilibrium. The only way that the correct limit can be approached as $t \rightarrow \infty$ is if

$$\sum_{j=1}^{N} f_{ne}^{(j)} = 1 \quad (44)$$

Using eq 44 in eq 43, one obtains the particularly simple result

$$\frac{dn_R}{dt} = -\frac{dn_C}{dt} = \frac{k_u}{[1 + n_m K_{eq}(1 - f_{ne})]} n_C - \frac{k_u K_{eq}}{[1 + n_m K_{eq}(1 - f_{ne})]} n_m n_R \quad (45)$$

Equation 45 is the extension, for pseudo-first-order reactions, of the Smith et al. result to conditions where $f_{ne} \neq 1$. The parameter $\gamma \equiv n_m K_{eq}(1 - f_{ne})$ plays a key role. It is typically a very small number. At low temperatures, f_{ne} is so close to unity that $1 - f_{ne}$ is difficult to compute accurately. At high temperatures, where $1 - f_{ne}$ begins to deviate significantly from zero, the factor $n_m K_{eq}$ (an effective, pseudo-first-order equilibrium constant) is so small that γ becomes even smaller than it is at low temperatures. Consequently, to a good approximation, $k_d = k_u$ and $k_{add} = k_d K_{eq}$ even when $f_{ne} \neq 1$. Approximating the dissociation rate coefficient as a unidirectional flux coefficient and calculating the reverse association rate coefficient from detailed balance is almost universally valid, as long as we understand that these rate coefficients may apply only to the very last (perhaps inconsequential) stage of the reaction.

The analysis described above has two intriguing features. First, $k_d = k_u/[1 + n_m K_{eq}(1 - f_{ne})]$ and $k_{add} = k_u K_{eq}/[1 + n_m K_{eq}(1 - f_{ne})]$ are composition dependent (through n_m). However, this composition dependence is so weak that it is unlikely to be detectable under ordinary experimental conditions. More interestingly, when f_{ne} begins to deviate from unity, eq 44 indicates that higher-order eigenvectors compensate so that detailed balance is satisfied exactly. This suggests correctly that $f_{ne} \neq 1$ indicates that some part of the reaction occurs as part of the vibrational−rotational relaxation process.

While f_{ne} is not a measure of the degree to which detailed balance is satisfied by k_d and k_{add}, it is nevertheless an important parameter. It measures the extent to which dissociation keeps collisional processes from establishing thermal equilibrium in the dissociating molecules. It is also the fractional contribution to k_{add} of the slowest-relaxing eigenmode of the system, so that $1 - f_{ne}$ is the fractional contribution to k_{add} of the IEREs.[92]

In their landmark text on unimolecular reactions,[91] Gilbert and Smith, p 304, suggest that detailed balance is not a well established physical law for association/dissociation reactions outside the high-pressure limit. We hope that we have corrected that misconception, which ultimately is tied to confusing flux coefficients with rate coefficients. We prefer the statement made by O. K. Rice in his seminal 1961 paper,[80] "...if unambiguous reaction rate constants can be found, then the quotient of the experimentally determined constants will give the equilibrium constant."

Concluding Remarks

Combustion chemistry, probably more so than other fields, relies heavily on theory for kinetic and thermochemical information. Typically, for any elementary reaction, experimental data exist, at most, over narrow temperature and pressure ranges. From this information, one must infer the rate coefficient, $k(T,p)$, from 250 to 2500 K and from 10 Torr to 100 atm. To do so requires a reliable theoretical apparatus. For reactions over multiple, interconnected potential wells, we have now provided such an apparatus. Ultimately, one would like to extend the present formalism to two dimensions (with E and J being the independent variables), but until that is done, the one-dimensional methodology discussed here appears to be quite satisfactory. Actually, the extension to two dimensions of the formalism for obtaining rate coefficients from the solution to the ME should be straightforward.

The dissociation of weakly bound free radicals at high temperatures is another important issue for combustion chemistry. The result that one can, under virtually all conditions, calculate the dissociation rate coefficient from an irreversible master equation (for single-well problems), and the reverse association rate coefficient from detailed balance, means that we can use our approximate 2-D solution of the master equation almost universally. However, it is necessary to realize that these rate coefficients apply only to the last stage of the reaction. When f_{ne} deviates significantly from unity, reaction interferes significantly with the collisional processes that try to establish thermal equilibrium, and some of the reactant is consumed as part of the internal-energy relaxation process.

For a given bond energy, f_{ne} gets smaller as the temperature gets higher and the size of the dissociating molecule gets larger. The ultimate limit is the situation discussed by Tsang et al.,[93] where the peak of the thermal energy distribution lies well above the dissociation threshold. The last stage of the reaction still obeys a phenomenological rate law with rate coefficients that satisfy detailed balance in such cases. However, so little of the reactant is consumed in this stage that the point is moot. The redeeming feature of this situation is that the molecule dissociates so rapidly that the rate is largely irrelevant; only the product distribution is important.

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