

 Open access • Journal Article • DOI:10.1063/1.455783

The relationship between recombination, chemical activation and unimolecular dissociation rate coefficients — [Source link](#)

[Sean C. Smith](#), [Murray J. McEwan](#), [Robert G. Gilbert](#)

Published on: 01 Apr 1989 - [Journal of Chemical Physics](#) (American Institute of Physics)

Topics: [Reaction rate constant](#), [Master equation](#) and [Dissociation \(chemistry\)](#)

Related papers:

- [Theory of Unimolecular and Recombination Reactions](#)
- [Theory of thermal unimolecular reactions at low pressures. I. Solutions of the master equation](#)
- [Theory of Thermal Unimolecular Reactions in the Fall-off Range. II. Weak Collision Rate Constants](#)
- [Theory of chemically activated unimolecular reactions. Weak collisions and steady states](#)
- [Angular momentum conservation in unimolecular and recombination reactions](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/the-relationship-between-recombination-chemical-activation-e5aohjlay1>

The relationship between recombination, chemical activation and unimolecular dissociation rate coefficients

Sean C. Smith, Murray J. McEwan, and Robert G. Gilbert

Citation: *The Journal of Chemical Physics* **90**, 4265 (1989); doi: 10.1063/1.455783

View online: <http://dx.doi.org/10.1063/1.455783>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/90/8?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[The dissociation/recombination reaction \$\text{CH}_4 \(+\text{M}\) \rightleftharpoons \text{CH}_3 + \text{H} \(+\text{M}\)\$: A case study for unimolecular rate theory](#)
J. Chem. Phys. **136**, 214309 (2012); 10.1063/1.4717706

[Vibrationally resolved rate coefficients and branching fractions in the dissociative recombination of \$\text{O}_2^+\$](#)
J. Chem. Phys. **122**, 014302 (2005); 10.1063/1.1825991

[The dissociative recombination rate coefficients of \$\text{H}^+\$, \$\text{HN}^+\$, and \$\text{HCO}^+\$](#)
J. Chem. Phys. **92**, 6492 (1990); 10.1063/1.458594

[Relation of rate coefficients for thermal unimolecular reactions to those for chemical activation](#)
J. Chem. Phys. **81**, 3745 (1984); 10.1063/1.448092

[Temperature Dependence of the \$\text{NO}^+ + e\$ Dissociative-Recombination-Rate Coefficient](#)
Phys. Fluids **11**, 904 (1968); 10.1063/1.1692018



NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP | Applied Physics
Reviews

The relationship between recombination, chemical activation and unimolecular dissociation rate coefficients

Sean C. Smith and Murray J. McEwan

Department of Chemistry, University of Canterbury, Christchurch 1, New Zealand

Robert G. Gilbert

School of Chemistry, University of Sydney, New South Wales 2006, Australia

(Received 7 September 1988; accepted 1 December 1988)

A new solution to the master equation relating the rate coefficients for unimolecular, recombination (association) and chemical activation reactions, incorporating weak collision effects, is presented. The solution establishes conditions for the validity of the commonly used procedure of relating the recombination rate coefficient, throughout the falloff regime, to the reverse single-channel unimolecular rate coefficient via the equilibrium constant. In addition, a relationship between the rate coefficient for stabilization in a chemical activation reaction and the reverse multichannel unimolecular dissociation rate coefficient is derived. This result, in conjunction with recently developed methods for fully incorporating angular momentum conservation into the solution of the master equation for unimolecular dissociation, enables both angular momentum and weak collision effects to be accurately incorporated into the solution of the master equation for chemical activation reactions in the falloff regime.

Application of this method to a typical ion/molecule chemical activation reaction, that of CH_3^+ with NH_3 , illustrates the importance of weak collision and angular momentum effects in this system.

I. INTRODUCTION

A reaction between two species A and B which proceeds through a collision complex AB^* may be classified as either a recombination (association) reaction (in which AB^* can dissociate only to produce reactants A and B) or a chemical activation reaction (in which AB^* can dissociate to produce other products as well). Both types of reaction exhibit the characteristic falloff behavior of unimolecular reactions, in which there is competition between collisional (activation/deactivation) and reaction processes. Proper modeling of these processes increases the reliability of *a priori* prediction of data (and of extrapolation of data to different pressures and temperatures), and also enables one to obtain experimental information about collisional energy transfer between the bath gas and the molecule in question. Chemical activation, unimolecular and recombination processes obey essentially the same master equation with different initial conditions and/or number of channels.

Chemical activation rate coefficients

Rate coefficients in a chemical activation system can be predicted from a knowledge of the microscopic rates. The most common method of modeling these reactions has been to treat the collision complex population as being at steady state. In this method, the reactive influx to a given energy level of collision complex is exactly balanced by (1) dissociation back to reactants, (2) dissociation through any other "exit channels" which may exist, and (3) irreversible stabilization to form the molecular product. In the simplest treatments, the collisional stabilization process is modeled using the strong collision approximation.¹ This amounts to an assumption that every inelastic collision with a bath gas mole-

cule leads to irreversible stabilization of the collision complex, no matter how great the excitation of the complex. It is now recognized,² however, that use of the strong collision assumption can lead to gross error in many cases (e.g., when the reaction is carried out with monatomic or diatomic bath gases). A weak collision model for the collisional energy transfer, in which the probability of energy transfer is small for large differences between the final and initial energies, is much more physically realistic.³ Attempting to correct the strong collision approach by using a collision efficiency β provides a basis for comparison between systems but, when used to extrapolate data over a wide range of pressures or temperatures, can easily be incorrect by a factor of, e.g., 3, for typical systems.² Various other methods of accounting for weak collision effects within the steady-state framework have been utilized. Rabinovitch and co-workers⁴ have illustrated the use of various forms of weak collision probability distribution functions in a steady-state master equation approach which does not consider the molecular states below the dissociation threshold. Herbst⁵ utilizes an empirical stabilization rate coefficient which decreases exponentially as the energy of the collision complex above the dissociation threshold increases. All of these approximate steady-state methods have in common the assumption that collisional stabilization is irreversible (i.e., all collisions resulting in activation from below the threshold may be neglected).⁶ As has been pointed out,⁷ however, neglect of activating collisions can lead to significant errors, particularly at lower pressures where collisional processes become rate determining. Larson *et al.*¹ have suggested an approximate means by which such collisional activation may be accounted for within the limits of the steady state, strong collision approach. A more complete master equation treatment, which considers

all energy states of the molecule and includes the effect of activating collisions, is required.

Relation between unimolecular and recombination rate coefficients

In a pioneering theoretical study of nonequilibrium recombination of atoms and the corresponding dissociation of diatomics, Keck and Carrier⁸ presented an approximate proof that the rate coefficients for recombination and dissociation are related by the equilibrium constant. The usual approach to calculating recombination rate coefficients (with proper account for weak collision effects) has therefore been^{9,10} to calculate first the rate coefficient for the reverse single-channel unimolecular dissociation at the appropriate pressure. The recombination rate coefficient is then determined from the dissociation rate coefficient and the equilibrium constant. However, as far as we are aware, this relationship between the rate coefficients for recombination and dissociation has never been rigorously proven using a general master equation involving both collisional transitions and microscopic rate coefficients for dissociation and recombination. A similar relationship between the rate coefficient for stabilization in a chemical activation reaction and that for the reverse multichannel dissociation reaction has recently been inferred by Larson *et al.*¹ on the basis of strong collision modeling, but again not rigorously proven. Quack¹¹ has provided an exact relationship between the forward and reverse rates for unimolecular *isomerization* (Valance and Schlag¹² had also considered this problem), but it will be seen that the unimolecular *dissociation* case is different.

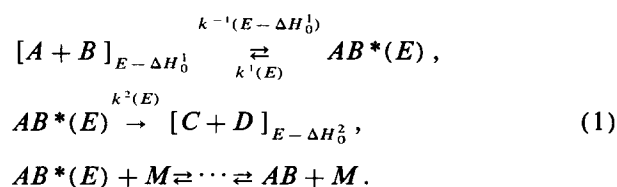
Schranz and Nordholm,⁷ in an exact master equation analysis of chemical activation reactions with a constant reactive influx, showed that the rate coefficient for stabilization, and hence the dissociation/stabilization ratio, could be obtained by evaluating the expansion coefficients of the reactive influx vector in terms of eigenvectors of the collisional/reactive matrix which appears in the solution of the master equation for thermal unimolecular dissociation. In the present paper we generalize their approach to the case of a time-dependent reactive influx (i.e., the reactant populations vary with the progress of reaction). By invoking microscopic reversibility for the reactive influx, we show that this gives a direct connection between the rate coefficient for stabilization and the rate coefficient for the corresponding unimolecular dissociation. The relationship derived also verifies the common practice of relating a recombination rate coefficient to the reverse unimolecular dissociation rate coefficient via the equilibrium constant at all pressures (e.g., Refs. 9 and 10). The derivations show that the problem of calculating stabilization rate coefficients in recombination or chemical activation reactions is entirely equivalent to that of calculating the reverse single-channel or multichannel unimolecular dissociation rate coefficients. Hence, recently developed methods of solving the two-dimensional master equation (in energy E and angular momentum J) for single-channel and multichannel unimolecular dissociation reactions¹³⁻¹⁵ may be applied to solve the corresponding recombination and chemical activation problems. For the latter, the relation-

ship derived therefore provides a new and powerful means of incorporating weak collision and angular momentum effects into the calculation of stabilization rate coefficients without the use of any steady-state approximations or treatments such as the Waage-Rabinovitch method¹⁶ which invoke the unphysical strong-collision approximation.

For sample calculations using the present method, we choose an ion/molecule chemical activation reaction which has been the subject of several experimental and theoretical studies:^{17-19,5} that of CH_3^+ with NH_3 in a helium bath gas. Estimates of the average downward internal energy transfer, $\langle \Delta E_{\text{down}} \rangle$, and the average downward rotational energy transfer, $\langle \Delta R_{\text{down}} \rangle$, may be made by modeling the pressure dependence of the stabilization rate coefficient. Comparison of the present calculations with those based on the strong collision assumption, and with those obtained by solution of the master equation without conservation of angular momentum in the falloff regime, shows the sensitivity of this system to proper incorporation of weak collision and angular momentum effects.

II. SOLUTION OF THE MASTER EQUATION FOR RECOMBINATION AND CHEMICAL ACTIVATION SYSTEMS

We consider a system in which thermalized reactants A and B , with total populations $A(t)$ and $B(t)$, collide to form a collision complex AB^* which may either form the stable molecule AB by collisions with an inert bath gas M , or dissociate via one or more channels. The reaction scheme is indicated in Eq. (1):



Here ΔH_0^i is the enthalpy difference between the products of channel i and the molecule AB at 0 K, $k^i(E)$ is the microscopic dissociation rate for channel i , and $k^{-1}(E - \Delta H_0^i)$ is the microscopic bimolecular rate coefficient for formation of the molecule at energy E from reactants A and B . If there is only one dissociative channel for the collision complex (that leading back to reactants), then the master equation describes a recombination reaction. Unimolecular dissociation is the reverse process to that represented in Eq. (1): one starts with a population of molecules AB which are excited by collisions and may then dissociate to give products $A + B$, $C + D$, etc. The master equation describing the rate of formation and loss of the molecular population at energy E and time t , denoted $g(E, t)$ is written

$$\begin{aligned}
 \partial g(E, t) / \partial t &= \omega \int [P(E, E')g(E', t) - P(E', E)g(E, t)] dE' \\
 &\quad - k(E)g(E, t) + k^{-1}(E - \Delta H_0^i) \\
 &\quad \times f_r(E - \Delta H_0^i)A(t)B(t), \quad (2)
 \end{aligned}$$

where ω is the collision frequency of the molecule with the bath gas, $P(E, E')$ is the probability of molecular energy

transfer from energy E' to energy E on collision with the bath gas, and $k(E) = \sum_i k^i(E)$ is the total microscopic unimolecular rate coefficient for reaction from energy E . We refer to the dissociative channel leading back to reactants as channel 1. For purposes of clarity, we deal only with the one-dimensional master equation in energy, though the appropriate generalization allows the two-dimensional master equation in energy and angular momentum to be treated similarly. $f_r(E - \Delta H_0^1)$ is the (normalized) thermal equilibrium population of reactants:

$$f_r(E) = \rho_r(E) \exp(-E/k_B T) / Q_r,$$

where $\rho_r(E)$ is the total density of states of A and B (including the relative translational and separate rotational degrees of freedom), and Q_r is the corresponding partition function for reactants. The above form for f_r for the populations of A and B invokes the assumption that A and B both undergo many more nonreactive collisions than reactive ones; this is usually an excellent approximation, particularly in the common situation where both are dilute in a bath gas. Equation (2) includes all energy levels of the molecule: those of the stable AB and those of the unstable collision complex AB^* . $A(t)$ and $B(t)$ are related to $g(E, t)$ by mass conservation: $A(t) = A(t=0) - \int g(E, t) dE$, etc. The other main class of unimolecular reactions, isomerization, has been considered in detail by Quack;¹¹ the essential difference between isomerization and dissociation/recombination is that in the latter case, the separate moieties are in thermal equilibrium, whence the term f_r in Eq. (2).

We note that $k^1(E)$ and $k^{-1}(E - \Delta H_0^1)$ are exactly related by microscopic reversibility:

$$k^1(E) \rho(E) = k^{-1}(E - \Delta H_0^1) \rho_r(E - \Delta H_0^1), \quad (3)$$

where $\rho(E)$ is the molecular density of states; the corresponding molecular partition function is $Q = \int b(E) dE$, where the (unnormalized) population $b(E) = \rho(E) \exp(-E/k_B T)$. Equation (2) may therefore be rewritten as

$$\begin{aligned} \partial g(E, t) / \partial t \\ = \omega \int [P(E, E') g(E', t) - P(E', E) g(E, t)] dE' \\ - k(E) g(E, t) + K_{\text{eq}} k^1(E) b(E) A(t) B(t) / Q, \end{aligned} \quad (4)$$

where K_{eq} is the equilibrium constant relating the equilibrium concentrations of reactants and molecule:

$$K_{\text{eq}} = [Q / Q_r] \exp(-\Delta H_0^1 / k_B T). \quad (5)$$

It is convenient to consider discrete states so that one may write Eq. (4) in matrix form:

$$dg(t) / dt = Jg(t) + K_{\text{eq}} \mathbf{r} A(t) B(t) / Q, \quad (6)$$

where J is the collisional/reactive matrix describing transitions between and reactive loss from the molecular populations, which are represented by the vector $\mathbf{g}(t)$:²⁰

$$\begin{aligned} J_{ij} &= \omega P(E_i, E_j), \quad i \neq j, \\ J_{ii} &= -[k(E_i) + \omega], \end{aligned} \quad (7)$$

and \mathbf{r} is the equilibrium reactive flux vector: $r_i = k^1(E_i) b(E_i)$. From the transformation²⁰ $\mathbf{g} = S\mathbf{c}$, where S is a diagonal matrix with elements $S_{ii} = [b(E_i)]^{1/2}$, Eq.

(6) is transformed into one involving an Hermitian matrix operator B :

$$dc(t) / dt = Bc(t) + K_{\text{eq}} \mathbf{u} A(t) B(t) / Q, \quad (8)$$

where $B = S^{-1} J S$ and $\mathbf{u} = S^{-1} \mathbf{r}$. Equation (8) has the formal solution²¹

$$\mathbf{c}(t) = \frac{K_{\text{eq}}}{Q} \int_0^t ds e^{B(t-s)} \mathbf{u} A(s) B(s), \quad (9)$$

where the initial condition $\mathbf{g}(t=0) = \mathbf{0}$ has been invoked. The vector \mathbf{u} may be expanded in terms of a complete set of orthogonal eigenvectors of the matrix B , $\{\psi_i\}$:

$$\mathbf{u} = \sum_i q_i \psi_i. \quad (10)$$

Substituting Eq. (10) into Eq. (9) yields

$$\mathbf{c}(t) = \frac{K_{\text{eq}}}{Q} \sum_i q_i \psi_i \int_0^t ds e^{\lambda_i(t-s)} A(s) B(s), \quad (11)$$

where λ_i is the eigenvalue corresponding to the eigenvector ψ_i . Now it has been established^{7,22} that in most cases the higher eigenvalues relax very quickly on an experimental timescale. This means that the terms for $i > 1$ in Eq. (11) reduce as follows:

$$\int_0^t ds e^{\lambda_i(t-s)} A(s) B(s) \approx \frac{A(t) B(t)}{|\lambda_i|}, \quad i > 1. \quad (12)$$

This is because for terms with $i > 1$ the integrand only takes any appreciable value when $A(s) B(s) \approx A(t) B(t)$ (note that all eigenvalues are negative, λ_1 being the least negative). Equation (11) therefore reduces to

$$\begin{aligned} \mathbf{c}(t) &= \frac{K_{\text{eq}}}{Q} \left[q_1 \psi_1 \int_0^t ds e^{-k_{\text{uni}}(t-s)} A(s) B(s) \right. \\ &\quad \left. + \left(\sum_i \frac{q_i}{|\lambda_i|} \psi_i - \frac{q_1}{k_{\text{uni}}} \psi_1 \right) A(t) B(t) \right], \end{aligned} \quad (13)$$

where we have identified $-\lambda_1$ as k_{uni} , the total rate coefficient for unimolecular dissociation through all channels. Now it is easily shown that

$$\sum_i \frac{q_i}{|\lambda_i|} \psi_i = -B^{-1} \mathbf{u}. \quad (14)$$

Furthermore, we may evaluate q_1 as

$$\begin{aligned} q_1 &= \psi_1 \cdot \mathbf{u} / \psi_1 \cdot \psi_1 = \mathbf{x}_1 \cdot S^{-2} \mathbf{r} / \mathbf{x}_1 \cdot S^{-2} \mathbf{x}_1 \\ &= \sum_i x_1(E_i) k^1(E_i) / \sum_i \{ [x_1(E_i)]^2 / b(E_i) \} \\ &= k_{\text{uni}}^{-1} \sum_i x_1(E_i) / \sum_i [x_1(E_i)^2 / b(E_i)], \end{aligned} \quad (15)$$

where \mathbf{x}_1 is the nonequilibrium eigenvector of J corresponding to the eigenvalue $\lambda_1 = -k_{\text{uni}}$ ($\mathbf{x}_1 = S\psi_1$), whose i th element is $x_1(E_i)$, and where k_{uni}^{-1} is the unimolecular rate coefficient for dissociation of the molecule through channel 1 (i.e., that leading to species A and B). Substituting Eqs. (14) and (15) into Eq. (13) and multiplying through by S gives

$$\begin{aligned} \mathbf{g}(t) &= \frac{K_{\text{eq}}}{Q} \left\{ k_{\text{uni}}^{-1} \frac{\sum_i x_1(E_i)}{\sum_i x_1(E_i)^2 / b(E_i)} \mathbf{x}_1 \right. \\ &\quad \left. \times \int_0^t ds e^{-k_{\text{uni}}(t-s)} A(s) B(s) \right\} \end{aligned}$$

$$+ \left[\eta - \frac{k_{\text{uni}}^1 \sum_i x_1(E_i)}{k_{\text{uni}} \sum_i x_1(E_i)^2 / b(E_i)} \mathbf{x}_1 \right] \times A(t)B(t) \quad (16)$$

where the vector η is defined by the equation

$$\eta = -J^{-1} \mathbf{r} \quad (17)$$

In Eq. (16), the molecular population splits into two terms. The first contributes mainly below the lowest dissociation threshold E_0^{min} (its distribution being governed by \mathbf{x}_1) and builds up with time at a rate which will be seen to be governed by k_{uni}^1 . This may be identified as the population of "stabilized" molecules $\mathbf{g}^s(t)$:

$$\mathbf{g}^s(t) = \frac{K_{\text{eq}}}{Q} \frac{k_{\text{uni}}^1 \sum_i x_1(E_i)}{\sum_i x_1(E_i)^2 / b(E_i)} \mathbf{x}_1 \times \int_0^t ds e^{-k_{\text{uni}}(t-s)} A(s)B(s) \quad (18)$$

The second term in Eq. (16) is at steady state with the population of reactants. Further examination will show that (a) it constitutes a very small part of the molecular population and (b) it contributes mostly above the dissociation threshold. It may be identified (see the Appendix) as the steady-state population distribution of the collision complex $\mathbf{g}^*(t)$:

$$\mathbf{g}^*(t) = \frac{K_{\text{eq}}}{Q} \left[\eta - \frac{k_{\text{uni}}^1 \sum_i x_1(E_i)}{k_{\text{uni}} \sum_i x_1(E_i)^2 / b(E_i)} \mathbf{x}_1 \right] A(t)B(t) \quad (19)$$

Note that the long time limit of the molecular population distribution $\mathbf{g}(t)$ defined in Eq. (16) is a steady-state distribution for which the net rate of formation of molecules is zero, such as that attained at long times in the reactive system. Summing Eq. (16) over all energies, we obtain the result

$$G(t) = \left[K_{\text{eq}} k_{\text{uni}}^1 f_{ne} \int_0^t ds e^{-k_{\text{uni}}(t-s)} A(s)B(s) \right] + K_{\text{eq}} \left(\frac{\sum_i \eta(E_i)}{Q} - \frac{k_{\text{uni}}^1 f_{ne}}{k_{\text{uni}}} \right) A(t)B(t) = G^s(t) + G^*(t) \quad (20)$$

where $G(t)$ is the total population of the molecule, $G^s(t) = \sum_i g^s(E_i, t)$ is the population of the stabilized complex, $G^*(t) = \sum_i g^*(E_i, t)$ and f_{ne} is defined as

$$f_{ne} = \left[\sum_i x_1(E_i) \right]^2 / Q \sum_i [x_1(E_i)^2 / b(E_i)] \quad (21)$$

The total rate of formation of the molecule is therefore given by

$$dG(t)/dt = K_{\text{eq}} k_{\text{uni}}^1 f_{ne} A(t)B(t) - k_{\text{uni}} G^s(t) + dG^*(t)/dt \quad (22)$$

Equations (20) and (22), together with the conservation of mass relations for $A(t)$ and $B(t)$, $A(t) = A(t=0) - G(t)$, etc., completely specify the time evolution of the system. However, Eq. (22) can be simplified: since the population of collision complex is very small and varies only slowly compared with the rate of formation of stable molecules, we

may neglect the third term in Eq. (22). The second term is the reverse reaction, since G^s is the population of stabilized molecules. The first term in Eq. (22) then serves to define the stabilization rate coefficient k_s , in terms of the rate coefficient for the reverse unimolecular dissociation, the equilibrium constant relating the equilibrium concentrations of the reactants and the molecular product, and the factor f_{ne} , as

$$k_s = K_{\text{eq}} k_{\text{uni}}^1 f_{ne} \quad (23)$$

Although f_{ne} is easily calculated, this is usually unnecessary, since $f_{ne} = 1$ to an excellent approximation (with the possible exception of reactions at very high temperatures where f_{ne} may become significantly less than unity).

Having determined the molecular population distribution as in Eq. (16), it is possible to calculate k_d , the rate of dissociation into each of the product channels. Assuming the system is far from equilibrium, the contribution from the population $\mathbf{g}^s(t)$ is negligible and the rate of dissociation through the i th channel is given by the integral (or, in the discretized case, the sum) over energy of $k^i(E)g^*(E, t)$:

$$k_d^i A(t)B(t) = \frac{K_{\text{eq}}}{Q} A(t)B(t) \left(\sum_j k^i(E_j) \eta(E_j) - \left\{ \frac{k_{\text{uni}}^1 \sum_j x_1(E_j)}{k_{\text{uni}} \sum_j [x_1(E_j)^2 / b(E_j)]} \right\} \sum_j k^i(E_j) x_1(E_j) \right) = k_{ss}^i A(t)B(t) - (K_{\text{eq}} k_{\text{uni}}^1 f_{ne} k_{\text{uni}}^i / k_{\text{uni}}) A(t)B(t) \quad (24)$$

where k_{ss}^i is the rate coefficient for dissociation through channel i if the system were at steady state (i.e., net rate of formation of molecules = 0). Note that, due to mass conservation, at steady state the total rate of dissociation equals the capture rate, hence $\sum_i k_{ss}^i = k_{\text{cap}} = k_{\text{rec}}^{\infty}$, the high-pressure recombination rate coefficient. k_{uni}^i is the multichannel unimolecular rate coefficient for dissociation through channel i , with $\sum_i k_{\text{uni}}^i = k_{\text{uni}}$. Hence, the rate coefficient through the i th channel is

$$k_d^i = k_{ss}^i - k_s k_{\text{uni}}^i / k_{\text{uni}} \quad (25)$$

An important constraint is that of mass balance:

$$\sum_i k_d^i + k_s \equiv k_{\text{cap}} = k_{\text{rec}}^{\infty} \quad (26)$$

Substituting Eqs. (23) and (25) into Eq. (26) shows that this constraint is indeed satisfied. Equation (25) and supporting relations enable quantities such as stabilization/deactivation ratios to be calculated. They are similar to, but contain terms missing from, the pioneering results of Rabinovitch and co-workers⁴ on chemical activation; these latter workers derived their results only for the steady-state case without considering states below the dissociation threshold.

In the case of a recombination reaction there are no products except for the molecule, and so the recombination rate coefficient is given by

$$k_{\text{rec}} = K_{\text{eq}} k_{\text{uni}}^1 f_{ne} \approx K_{\text{eq}} k_{\text{uni}} \quad (27)$$

where k_{uni} is the nonequilibrium rate coefficient for the reverse (single channel) unimolecular dissociation. Mass con-

ervation, together with Eq. (16), gives the precise evolution of the molecular population distribution in a recombination system until it attains eventual equilibrium with reactants. Note that K_{eq} in Eq. (27) is given by the partition function ratio at equilibrium [$Q = \int b(E)dE$, etc.], not the nonequilibrium population [i.e., $Q \neq \int x(E)dE$]. This is a major difference to the case for forward and reverse rate coefficients for isomerization, where the ratio $k_{forward}/k_{back}$ is dependent on pressure.¹¹

In summary, for a chemical activation system, the stabilization rate coefficient k_s is given by Eq. (23), where the k_{uni}^1 therein is obtained from

$$k_{uni}^1 = \int x_1(E)k^1(E)dE \int x_1(E)dE, \quad (28)$$

where the distribution function $x_1(E)$ is obtained from the solution of the integral eigenvalue relation:

$$-k_{uni}x_1(E) = \omega \int [P(E,E')x_1(E') - P(E',E)x_1(E)] \times dE' - k(E)x_1(E) \quad (29)$$

with $k(E) = \Sigma k^i(E)$. The dissociation rate through channels other than the entrance channel (the entrance channel being denoted as channel 1) is given by Eq. (25), wherein the rate coefficient k_{ss}^i is given by

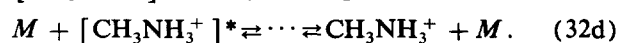
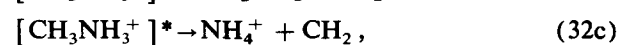
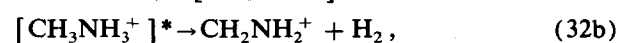
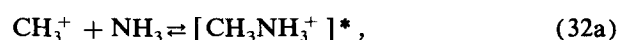
$$k_{ss}^i = (K_{eq}/Q) \int k^1(E)\eta(E)dE, \quad (30)$$

where the distribution $\eta(E)$ at energy E_i is given by (reverting to discrete notation for convenience) $\eta = -J^{-1}\mathbf{r}$, with $r_i = k^1(E_i)b(E_i)$. Matrix inversion to find J^{-1} is avoided by solving the set of linear simultaneous equations which are the discrete equivalent of

$$\omega \int [P(E,E')\eta(E') - P(E',E)\eta(E)]dE' - k(E)\eta(E) = -k^1(E)b(E). \quad (31)$$

III. APPLICATION TO THE $\text{CH}_3^+/\text{NH}_3$ CHEMICAL ACTIVATION REACTION

We illustrate the use of Eq. (23) by modeling experimental data for a typical ion/molecule chemical activation reaction: that of CH_3^+ with NH_3 in He bath gas. This reaction has been the subject of a number of experimental and theoretical studies. A low-pressure study at 300 K by Huntress *et al.*,¹⁷ using the ion cyclotron resonance (ICR) technique, revealed the presence of two exothermic dissociative channels, leading to the products CH_2NH_2^+ and NH_4^+ , respectively. No association (recombination) product was observed in the low-pressure study. A selected ion flow tube (SIFT) study at higher pressures by Smith and Adams¹⁸ revealed, in addition to the two dissociative channel products, the association product CH_3NH_3^+ :



They found that the association product accounted for about

20% of the total reaction and observed no pressure dependence in the range 0.2–0.7 Torr. Saxer *et al.*¹⁹ studied this reaction in a selected ion drift tube (SIDT) with the mean relative kinetic energy between reactants ranging from 4.5 to 19 kJ mol⁻¹. The lowest value corresponds to an essentially thermal system and produced results in accord with earlier measurements.¹⁸ Their data covered a wider pressure range, however, and they observed significant pressure dependence of the association rate coefficient.

Herbst⁵ has presented a theoretical study of this reaction, using RRKM parameters calculated by Nobes and Radom,²³ which illustrated the effect on the predicted rate coefficients of angular momentum conservation, the dipole moment of ammonia, and the barrier height of the major exit channel [Eq. (32b)]. The model used by Herbst involved calculating the steady-state population of the excited collision complex with a given total energy E and angular momentum J . Microscopic rate coefficients for the reactive influx and its reverse dissociation were calculated using the phase space approach of Chesnavich and Bowers.²⁴ In this approach, the two moieties in the transition state are treated as free rotors acting under the influence of a central potential. The microscopic rate coefficients for the major dissociation channel, Eq. (32b), were calculated using RRKM theory. Collisional stabilization was modeled using a particular form of "relaxation rate coefficient" k_{rel} , which is a function of the excess internal energy of the complex above the lowest dissociation threshold. This model has two important deficiencies. The effect of the dipole moment of ammonia is identified as being primarily to increase the range of angular momenta which can lead to reaction because of the long-range ion-dipole potential. However, the fact that the long-range ion-dipole potential is noncentral is neglected in applying the phase space²⁴ approach. As has been discussed previously by several authors,^{25,26,15} the ensuing hindrance of the dipole rotation causes the density of states at the transition state to be substantially reduced, thus reducing the predicted reactive influx. In order to compensate for this deficiency, Herbst was forced to use an "effective dipole moment" of 0.3 Debye, which is much smaller than the actual dipole moment of 1.47 Debye. The second deficiency is in the treatment of collisional effects. The correct way to incorporate weak collision effects is by the solution of the master equation [Eq. (1), or its two-dimensional equivalent in E and J]. The model used by Herbst assumes that collisional stabilization below the threshold is irreversible, thus neglecting activating collisions. As has been pointed out previously,⁷ this can lead to significant error. In addition, the accuracy of using k_{rel} such as that suggested by Herbst to mimic weak collision effects can only be tested by carrying out an exact solution to the problem.

In a recent paper¹⁵ we have presented efficient and accurate means by which the effect of the noncentral ion-dipole potential and also the effect of angular momentum conservation may be incorporated into the master equation for unimolecular dissociation. The relevant equations for our solution of the two-dimensional master equation are contained therein. The generalization of these equations to the present multichannel calculation proceeds in a manner entirely anal-

ogous to that required for the simpler treatment which we have shown may be used for most neutral reactions.¹⁴ The use of Eq. (23) in conjunction with these allows the problems with the Herbst model to be obviated.

Since reaction (32c) contributes only fractionally to the product branching ratio,^{18,19} we assume that this reaction produces a negligible perturbation to the falloff of the stabilization rate coefficient and so may be neglected in the calculations. The structure and vibrational frequencies assumed for the molecule CH_3NH_3^+ and the transition state for the elimination of H_2 [Eq. (32b)] are those used by Herbst,⁵ calculated by Nobes and Radom²³ (vibrational frequencies calculated with the techniques used by these authors are expected to be quite accurate for the present purposes, provided a correction factor of 0.9 is applied). The vibrational frequencies for the simple fission transition state [reaction (32a)] are taken as those of the separate reactants.^{23,27} The potential of interaction between the moieties in the simple fission transition state is that between the positive charge of the methyl cation and the dipole and isotropic polarizability of ammonia [1.47 Debye²⁸ and $2.26 \times 10^{-24} \text{ cm}^3$ (Ref. 29), respectively]. The separation of the moieties in the simple fission transition state was determined by canonical variation³⁰ (this is now a routine technique, wherein one uses the same transition state for all E and J , with the separation between the moieties chosen, at a given temperature, to produce the minimum overall capture rate). The (high-pressure limiting) capture rate so calculated, using ordinary RRKM theory (with appropriate modification for the hindered-dipole rotation¹⁵) for $k(E, J)$, is $5.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

Two improvements to this method of treating the simple fission transition state would be as follows: (1) to use microcanonical variational transition-state theory [in which a different separation of the moieties may be chosen for each E and J , the criterion for selection being to minimize $k(E, J)$]^{25,31,32} and (2) to make allowance for poor coupling of some internal degrees of freedom in ion/molecule systems where the transition state is at very large separations.^{25,26,33} Chesnavich *et al.*²⁵ have incorporated these improvements into a simplified microcanonical variational model for the calculation of capture rates in ion/molecule reactions which predicts the capture rate for the $\text{CH}_3^+/\text{NH}_3$ system to be $2.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. We conclude from the significant discrepancy between the two capture rates that a microcanonical variational treatment with uncoupling of appropriate internal degrees of freedom at the long range, orbiting transition state would be necessary if a more exact treatment were required. Such a calculation is in progress and will be presented in a later paper.³³ Given the illustrative purposes of our present calculations, we have chosen at this stage simply to apply the RRKM canonical variational treatment. Note that the methods of Chesnavich *et al.*²⁵ and Troe,²⁶ because they deal only with degrees of freedom that are important on the long-range ion-dipole potential surface, are limited to calculation of the high-pressure limit of the stabilization rate coefficient.

For the falloff calculation, full account was taken of angular momentum conservation.¹³⁻¹⁵ This involves solving a two-dimensional master equation for unimolecular dissociation

with independent variables being the energy of the active degrees of freedom E (one active external rotor plus all internal degrees of freedom) and the angular momentum J . The two-dimensional master equation in E and J is first transformed into one involving the active internal energy E and the rotational energy R for the two inactive external rotational degrees of freedom.^{9,13} The resulting equation is reduced by a first-order perturbational technique¹⁵ to a one-dimensional J -averaged master equation in the internal energy E alone, which is solved exactly by numerical means.¹³ The probability distribution functions for internal energy transfer, $P(E, E')$, and external (inactive) rotational energy transfer, $p(R, R')$ (R being the rotational energy), were both approximated by an exponential-down form:

$$P(E, E') \propto \exp[(E - E') / \langle \Delta E_{\text{down}} \rangle],$$

$E < E'$, etc. The falloff curve is not strongly dependent on the form of $P(E, E')$ as long as it is physically reasonable, and it has been shown¹³ that an exponential-down form for $p(R, R')$ is physically correct for an ion/molecule system; upward rates were given by microscopic reversibility. The method of solution of the master equation was that appropriate for an ion/molecule system.¹⁵ The collision frequency ω for collisions of $[\text{CH}_3\text{NH}_3]^+$ with He was taken to be that given by the Langevin ion/induced dipole result, leading to $\omega = 4.07 \times 10^7 (p/T) \text{ s}^{-1}$, where p is the pressure of He (Pa) and T the temperature (K).

The RRKM parameters for the two channels are presented in Table I. Figure 1 gives a schematic illustration of the profile of the potential surface along the reaction coordinate and shows the relevant threshold energies used in the calculation. The threshold for dissociation of CH_3NH_3^+ back to reactants is taken to be 442 kJ mol^{-1} (Ref. 23). The barrier height for the dissociating channel leading to products [Eq. (32b)] is taken as 348 kJ mol^{-1} . This barrier height is slightly lower than that predicted by Nobes and Radom²³ (367 kJ mol^{-1}). It was found, however, that the experimental falloff data could not be fitted using a barrier height of 367 kJ mol^{-1} unless the average internal and rotational energy transfer parameters $\langle \Delta E_{\text{down}} \rangle$ and $\langle \Delta R_{\text{down}} \rangle$ were assumed to have values which were too small ($< 100 \text{ cm}^{-1}$) to be physically reasonable. Previous work^{15,34} indicates that the values of these quantities should be of the order of $0.5k_B T - 1.5k_B T$ ($100 - 300 \text{ cm}^{-1}$ at 300 K) for this type of system. In the absence of further knowledge about the relative sizes of these two parameters, we chose to assign the same value for both of them, and vary the magnitude of this value in order to reproduce the experimental data. The values of $\langle \Delta E_{\text{down}} \rangle$ and $\langle \Delta R_{\text{down}} \rangle$ used for the calculated curve in Fig. 2 are both $0.75k_B T$ (156 cm^{-1}), which allow an excellent fit of the experimental data when used in conjunction with a barrier height for the exit channel of 348 kJ mol^{-1} .

The calculated pressure dependence of the stabilization rate coefficient k_s for the reaction at 300 K is shown in Fig. 2 (curve A), along with the experimental falloff data for the reaction obtained by Saxer *et al.*¹⁹ Curve B is that resulting from use of the strong collision assumption: it includes angular momentum conservation but does not include weak colli-

TABLE I. RRKM parameters for multichannel dissociation of $(\text{CH}_3\text{NH}_3)^+$. (A) Molecular vibrational frequencies and rotational constants for $(\text{CH}_3\text{NH}_3)^+$. Frequencies (appropriately scaled) and structure from Nobes and Radom (Ref. 23). (B) Frequencies and rotational constants for transition states of Eqs. (32a) and (32b). For simple fission transition state (32a), rotational constant for hindered dipole rotation (Ref. 15) marked with an asterisk. Frequencies and structure of CH_3^+ from Nobes and Radom (Ref. 23). Potential of interaction along reaction coordinate for (32a) taken as $V(r) = -6.9492 \times 10^{26} \alpha/r^4 - 289.21 \mu/r^2$ kJ mol $^{-1}$, with $\alpha = 2.26 \times 10^{-24}$ cm 3 , $\mu = 1.47$ Debye, r in Å.

			(A)	
Vibrations:			Rotations	
Frequencies ^a (cm $^{-1}$)			Type	B values ^b (cm $^{-1}$)
275	(1)		External inactive	0.648 (1,2)
907	(1)		External active	2.725 (3,1)
1006	(2)			
1348	(2)			
1610	(1)			
1653	(2)			
1703	(1)			
1844	(2)			
3259	(1)			
3367	(2)			
3538	(1)			
3615	(2)			
			(B)	
Vibrations:			Rotations	
Frequencies ^a (cm $^{-1}$)			B values ^b (cm $^{-1}$)	
(32b)	(32a)	Type	(32b)	(32a)
452	(1)	950 (1) External inactive	0.646 (1,2)	0.0205 (1,2)
822	(1)	1628 (2) External active	2.269 (1,1)	2.543 (3,1)
1001	(1)	3337 (1) Internal		10.36 (3,1)
1061	(1)	3414 (2)		8.951 (2,2)
1093	(1)	1350 (1)		*9.301 (1,2)
1183	(1)	1370 (2)		
1388	(1)	2903 (1)		
1558	(1)	3090 (2)		
1562	(1)			
1731	(1)			
1805	(1)			
2106	(1)			
2517	(1)			
3299	(1)			
3403	(1)			
3701	(1)			
3821	(1)			

^a Degeneracies in parentheses.

^b Parenthetic quantities are symmetry number and dimension, respectively.

sion effects. An approximate method correcting curve B for weak collision effects is to calculate a value of β with physically reasonable values of $\langle \Delta E_{\text{down}} \rangle$ and $\langle \Delta R_{\text{down}} \rangle$ by using the relationship derived by Troe,⁹ which relates these quantities in the low-pressure limit. However, the Troe solution can overestimate β by a factor of 2 for typical ion/molecule reactions.¹⁵ While this error can be corrected,¹⁵ the Troe model is not readily extendable to multichannel reactions,¹⁴ as would be required in the present case (one needs a collision efficiency β_i which is specific to the reactant channel). Hence, the present method appears to be the only currently available means of accurately determining the stabilization rate coefficient in the falloff regime.

An alternative might be to determine a value of β which allows the strong collision curve to fit the experimental results over a limited pressure range (ca. 1 Torr) and then extrapolate to lower pressures. The value of β required to reproduce the experimental data in this way is 0.13. Extrapolating with this value of β to low pressures produces a curve which overestimates the rate coefficient by a factor of ca. 2. Therefore, the use of β to modify the strong collision curve does not allow reliable extrapolation of the data over a wide range of pressures. In this case such an error may not materially affect the predicted behavior of the system, since at low pressures dissociation of the collision complex is the dominant process, the rate of stabilization being negligible in

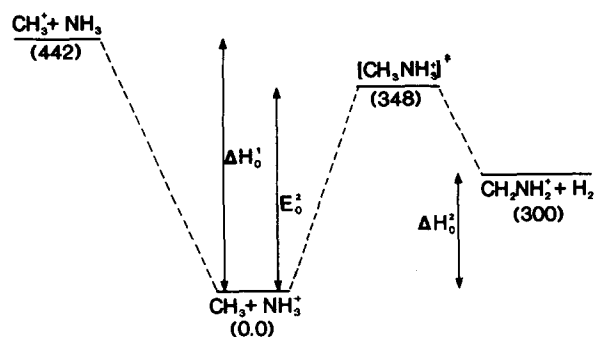


FIG. 1. Schematic diagram of potential surface along reaction coordinate for $\text{CH}_3^+/\text{NH}_3$ reaction, relative to $[\text{CH}_3\text{NH}_3]^+$ having energy 0.0 kJ mol^{-1} .

comparison. However, for reactions where the collision complex has a longer lifetime and hence association persists to low pressures, such an extrapolation will produce significant error.

The sensitivity of the solution to correct incorporation of angular momentum conservation is seen by comparing with results for k_s obtained by solution of the one-dimensional master equation without conservation of angular momentum in the falloff regime^{13,35} (the same $\langle \Delta E_{\text{down}} \rangle$ value is used, but $\langle \Delta R_{\text{down}} \rangle$ is not involved in the purely one-dimensional solution); these values were several orders of magnitude too small. It is apparent that correct accounting for both weak collision and angular momentum effects is essential in order to obtain an accurate fit to the data and to deduce information concerning energy transfer. The parameters which are most uncertain in the calculation are the average internal and rotational energy transfer per collision with the bath gas helium, and the barrier height for the exit channel. The lack of temperature-dependent data does not allow an unambiguous determination of both the barrier height for the exit channel and the average energy transfer parameters.

For the results shown in Fig. 2, f_{ne} was evaluated exactly at a number of pressures throughout the falloff regime. In

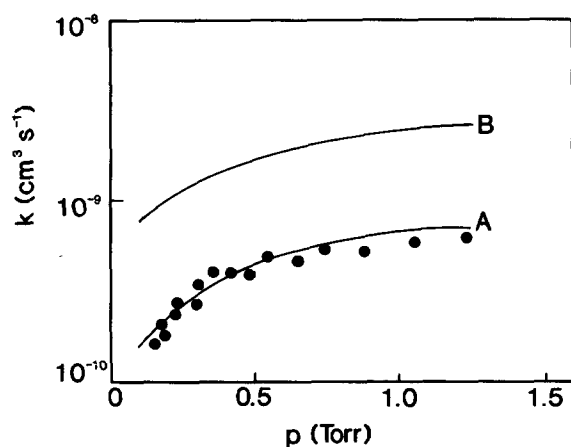


FIG. 2. Calculated pressure dependence of stabilization rate coefficient k_s (as ratio to high-pressure limiting value) for $\text{CH}_3^+/\text{NH}_3$ chemical activation reaction at 298 K; parameters as in the text. For conversion from unimolecular rate coefficients, $K_{\text{eq}} = 2.93 \times 10^{51} \text{ cm}^3$. A: master equation solution with full angular momentum conservation. B: strong collision calculation with J conservation. Points: data of Saxer *et al.* (Ref. 19).

all cases the value of f_{ne} was indistinguishable from 1. The approximation of setting f_{ne} equal to unity is therefore fully justified.

IV. CONCLUSIONS

The problem of predicting falloff behavior and modeling falloff data in recombination and chemical activation reactions is an important and fundamental one. Various approaches to this problem have been used, most of which treat the collisional stabilization process as irreversible, using a steady-state approximation to determine the collision complex populations.^{4,5} This neglects activation of stabilized molecules and can lead to significant error,⁷ particularly at lower pressures and high temperatures where the effect of activating collisions is most significant. Moreover, *a posteriori* corrections (such as the collision efficiency in the strong collision model) provide little more than a scale for qualitative comparison between systems and may lead to substantial error if used to extrapolate beyond the range of experimental data used to determine them.²

In order to overcome these problems one must solve the chemical activation/recombination master equation involving all states of the molecule, including those below the dissociation threshold.⁷ From this, we have shown that the rate coefficients for stabilization and for the reverse single-channel or multichannel unimolecular dissociation are directly related by an expression involving the equilibrium constant for the reaction and a "nonequilibrium" factor f_{ne} which is in most cases unity. This relationship, expressed for chemical activation reactions in Eq. (23) and for recombination reactions in Eq. (27), allows the use of the steady-state approximation to be avoided at no extra computational cost, since very efficient algorithms exist for the solution of the multichannel unimolecular master equation, with full angular momentum conservation if necessary.³⁶ (For most ion/molecule reactions, because of the long-range nature of the potential of interaction, including angular momentum conservation will be very important). A summary of the appropriate formulas is given at the end of Sec. II. Use of this method will lead to improved reliability of *a priori* prediction of chemical activation rate coefficients, and enables average energy transfer parameters for collisions between the product molecule and the bath gas to be determined in chemical activation systems by modeling experimental falloff data.

The analysis presented justifies the procedure (which, though not all new,⁸ has not previously been rigorously proven for reactions involving polyatomic species) of relating recombination rate coefficients to the reverse single-channel unimolecular dissociation rate coefficients by the equilibrium constant throughout the falloff regime. However, it shows that f_{ne} may become significantly less than unity at sufficiently high temperatures, a *caveat* which must be borne in mind when relating dissociation and recombination data over a very wide temperature range (e.g., Ref. 37).

ACKNOWLEDGMENTS

The support of the Australian Research Grants Scheme is gratefully acknowledged, as is that of a University Grants Committee Postgraduate Scholarship for SCS. We thank

Professor Sture Nordholm and Dr. Dave Golden for stimulating discussions.

APPENDIX: IDENTIFICATION OF THE COLLISION COMPLEX POPULATION DISTRIBUTION

The identification of $g^*(t)$ as the steady-state complex population proceeds as follows. First, we note that, from Eq. (17), the population distribution $K_{\text{eq}}A(t)B(t)\eta/Q$ is the solution $v(t)$ of the equation

$$Jv + K_{\text{eq}}rA(t)B(t)/Q = 0. \quad (\text{A1})$$

This is an equation for a steady-state molecular population distribution. Equation (A1) describes a steady-state distribution involving all molecular states for which the net rate of formation of molecules is zero, such as that attained at long times in the reactive system. For a recombination system, Eq. (A1) has solution $v = K_{\text{eq}}A(t)B(t)b/Q$ (in this case, the steady-state distribution is an equilibrium distribution). In the case of a chemical activation system, the energy distribution of $v(t)$, $v(E,t)$ in continuum notation, will be Boltzmann in nature at lower energies, but will deviate from Boltzmann at energies close to and above the lowest dissociative threshold. That v for a chemical activation system is still essentially a Boltzmann distribution at lower energies can be seen by noting that in Eq. (A1) $k(E) = 0$ for $E < E_0^{\text{min}}$ and so, for energies below the lowest dissociation threshold, Eq. (A1) becomes

$$\omega \int P(E, E')v(E')dE' - \omega v(E) = 0, \quad E < E_0^{\text{min}}. \quad (\text{A2})$$

Hence at energies sufficiently far below E_0^{min} the effect of the nonequilibrium nature of the populations close to and above E_0^{min} is negligible and Eq. (A2) will be satisfied by a distribution which is Boltzmann in nature. From Eqs. (14) and (A1), the steady state $v(t)$ may be expressed as

$$\begin{aligned} v(t) &= [K_{\text{eq}}A(t)B(t)/Q]\eta \\ &= -[K_{\text{eq}}A(t)B(t)/Q]SB^{-1}u \\ &= \frac{K_{\text{eq}}A(t)B(t)}{Q} \sum_i \frac{q_i}{|\lambda_i|} x_i, \end{aligned} \quad (\text{A3})$$

where x_i is the i th eigenvector of the J matrix. Since, from Eqs. (15) and (19), the population $g^*(t)$ contains all the terms in this expansion except that involving x_i , we see that $g^*(t)$ is the contribution to the steady state population distribution $v(t)$ of the higher eigenvectors, corresponding to the eigenvalues which relax much more quickly than λ_1 . In Eq. (19), $g^*(t)$ is represented as the difference between two vectors which are both essentially Boltzmann distributions at lower energies and only deviate from each other at energies close to and above E_0^{min} . This population distribution therefore contributes mainly above the threshold, is small in magnitude (since $|\lambda_2|^{-1}, |\lambda_3|^{-1}, \dots \ll |\lambda_1|^{-1}$), and is at steady state with the reactant population $A(t)B(t)$. Equation (19) constitutes a mathematical definition of the steady

state distribution of excited collision complexes. This completes the identification of $g^*(t)$ as the steady-state complex population.

¹See, for example, C. W. Larson, P. H. Stewart, and D. M. Golden, *Int. J. Chem. Kinet.* **20**, 27 (1988); L. M. Bass, P. R. Kemper, V. G. Anicich, and M. T. Bowers, *J. Am. Chem. Soc.* **103**, 5283 (1981).

²R. G. Gilbert, K. Luther, and J. Troe, *Ber. Bunsenges. Phys. Chem.* **87**, 169 (1983).

³D. C. Tardy and B. S. Rabinovitch, *Chem. Rev.* **77**, 369 (1977).

⁴G. H. Kohlmaier and B. S. Rabinovitch, *J. Chem. Phys.* **38**, 1692 (1963); D. W. Setser, B. S. Rabinovitch, and J. W. Simons, *ibid.* **40**, 1751 (1964).

⁵E. Herbst, *J. Chem. Phys.* **82**, 4017 (1985).

⁶M. Hoare, *J. Chem. Phys.* **38**, 1630 (1963).

⁷H. W. Schranz and S. Nordholm, *Chem. Phys.* **87**, 163 (1984).

⁸J. C. Keck and G. Carrier, *J. Chem. Phys.* **43**, 2284 (1965).

⁹J. Troe, *J. Chem. Phys.* **66**, 4745 (1977); *Z. Phys. Chem.* **154**, 73 (1987).

¹⁰R. G. Gilbert and M. J. McEwan, *Aust. J. Chem.* **38**, 231 (1985).

¹¹M. Quack, *Ber. Bunsenges. Phys. Chem.* **88**, 94 (1984).

¹²W. G. Valance and E. W. Schlag, *J. Chem. Phys.* **47**, 3276 (1967).

¹³S. C. Smith and R. G. Gilbert, *Int. J. Chem. Kinet.* **20**, 307 (1988).

¹⁴S. C. Smith and R. G. Gilbert, *Int. J. Chem. Kinet.* **20**, 979 (1988).

¹⁵S. C. Smith, M. J. McEwan, and R. G. Gilbert, *J. Chem. Phys.* **90**, 1630 (1989).

¹⁶E. V. Waage and B. S. Rabinovitch, *Chem. Rev.* **70**, 377 (1970).

¹⁷W. T. Huntress, R. F. Pinizzotto, and J. B. Laudenslager, *J. Am. Chem. Soc.* **95**, 4107 (1973).

¹⁸D. Smith and N. G. Adams, *Chem. Phys. Lett.* **47**, 145 (1977); **54**, 535 (1978).

¹⁹A. Saxer, R. Richter, H. Villinger, J. H. Futrell, and W. Lindinger, *J. Chem. Phys.* **87**, 2105 (1987).

²⁰E. W. Montroll and K. E. Shuler, *Adv. Chem. Phys.* **1**, 361 (1958).

²¹P. Ritger and N. Rose, *Differential Equations with Applications* (McGraw-Hill, New York, 1968).

²²E. E. Nikitin, *Theory of thermally induced gas-phase reactions* (Indiana University Press, New York, 1966); H. O. Pritchard, *Quantum Theory of Unimolecular Reactions* (Cambridge University Press, Cambridge, England, 1984), p. 24.

²³R. H. Nobes and L. Radom, *Chem. Phys.* **74**, 163 (1983).

²⁴W. J. Chesnavich and M. T. Bowers, *J. Am. Chem. Soc.* **98**, 8301 (1976); *J. Chem. Phys.* **66**, 2306 (1977).

²⁵W. J. Chesnavich, T. Su, and M. T. Bowers, *J. Chem. Phys.* **72**, 2641 (1980).

²⁶J. Troe, *Chem. Phys. Lett.* **122**, 425 (1985); *J. Chem. Phys.* **87**, 2773 (1987).

²⁷G. Herzberg, *Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1949).

²⁸A. L. McClellan, *Tables of Experimental Dipole Moments* (Freeman, San Francisco, 1963).

²⁹J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

³⁰B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.* **83**, 1052 (1979).

³¹See, for example, D. L. Bunker and M. Patengill, *J. Chem. Phys.* **48**, 772 (1968); W. L. Hase, *ibid.* **64**, 2442 (1976); in *Dynamics of Molecular Collisions (B)*, edited by W. H. Miller (Plenum, New York, 1976); D. G. Truhlar and B. C. Garrett, *Annu. Rev. Phys. Chem.* **35**, 159 (1984).

³²W. J. Chesnavich, *J. Chem. Phys.* **84**, 2615 (1986).

³³S. C. Smith, M. J. McEwan, and R. G. Gilbert (to be submitted).

³⁴N. Date, W. L. Hase, and R. G. Gilbert, *J. Phys. Chem.* **88**, 5135 (1984).

³⁵P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley, London, 1972).

³⁶S. C. Smith and R. G. Gilbert, Program FALLOFF, Quantum Chemistry Program Exchange, 1988.

³⁷K. Glänzer, M. Quack, and J. Troe, *16th International Symposium on Combustion* (Combustion Institute, Pittsburgh, 1977), p. 949.