Nonequilibrium Effects in Recombination-Dissociation Kinetics II

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The selfconsistent theory of recombination-dissociation kinetics developed in an earlier article is derived in a more rigorous manner. A noniterative solution is obtained for the resulting equations describing the nonequilibrium distribution of the internal molecular energy levels. This method of solving these equations also leads to a number of interesting mathematical and physical insights about the importance of nonequilibrium effects in recombination-dissociation kinetics. Implicit in these equations is a method for calculating the vibrational relaxation times for both recombination and dissociation reactions. These same equations also arise in calculating the rate constant for a nontrivial model of a dissociating diatomic molecule. The mathematical techniques used to derive this information also allows us to show that the selfconsistent theory is really a generalization of the conventional steady-state approximation and a special case of a projection operator formalism for solving problems in nonequilibrium statistical mechanics.

All of the existing theories of nonequilibrium effects in recombination-dissociation kinetics are based on the existence of two or more times cales which characterize the approach to equilibrium of a gas of recombining atoms and molecules undergoing dissociation. On the fast microscopic time scale or clock, the translational and internal degrees of freedom of the reactants and products immediately relax to a state of local equilibrium; over a longer period of time, which can be characterized by a slower clock or time scale, the reacting system slowly approaches therodynamic equilibrium[1–9]. Theories of recombination-dissociation kinetics based on the conventional steady-state approximation treat all molecules in vibrational states above the ground state as if they relax to a steady-state distribution in a period of time which is almost instantaneous compared to a typical reaction time[1–3]. Ross and Mazur's and Pyun and Ross's approach to this problem is to equate the fast time scale to the time required for the internal degrees of freedom of the diatomic molecule to relax to an equilibrium or Maxwell-Boltzmann distribution[8, 9]. These different assumptions about the fast time scale of a reacting system are responsible for the difference in the rate constants predicted by these theories. Since the rate constant for a reaction is supposedly unique, there should be a single formalism from which the existing theories can be derived. In a recent study, we made a start in this direction by deriving a selfconsistent theory that combines the best features of the steady-state approximation and the theory of Ross and Mazur[10]. Even though this theory takes advantage of the difference between vibrational and chemical relaxation times, its rate constants are very similar to those predicted by the conventional steady-state approximation. This raises two possibilities. Either the conventional steady-state approximation is valid only as long as the rate of reaction is less than the rate of relaxation, or it is possible to derive a nonequilibrium theory of recombination-dissociation kinetics without having to make any explicit references about the approach to equilibrium on the fast time scale. The purpose of the present study is to show that not only is the second choice correct, but it is possible to derive many of the existing theories from a steady-state approximation. The proof of this statement is almost trivial, once we uncover the very sophisticated approach to perturbation theory that is implicit in the selfconstistent theory as well as the work of Ross and Mazur, and Pyun and Ross. The following section contains a more mathematically rigorous derivation of the selfconsistent theory. In Section III, a number of mo-

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[1] E. V. Stupochenko and A. I. Osipov, Russ. J. Phys. Chem. **33**, 36 [1959].

[2] S. W. Benson and T. Fueno, J. Chem. Phys. **36**, 1597 [1962].

[3] J. W. Rich, Dissociation and Energy Transfer in Diatomic Molecular Systems, Ph. D. Thesis, Princeton University 1965.

[4] O. K. Rice, J. Phys. Chem. **65**, 1972 [1961]; **67**, 1733 [1963].

[5] C. A. Brau, J. C. Keck, and G. F. Carrier, Phys. Fluids **9**, 1885 [1966].

[6] J. Keck and G. Carrier, J. Chem. Phys. **43**, 2284 [1965].

[7] R. D. Levine, J. Chem. Phys. **46**, 331 [1967].

[8] J. Ross and P. Mazur, J. Chem. Phys. **35**, 19 [1961].

[9] C. W. Pyun and J. Ross, J. Chem. Phys. **40**, 2572 [1964].

[10] H. J. Kolker, J. Chem. Phys. **44**, 582 [1966].

dern approaches to perturbation theory are used to derive a nonequilibrium theory for the dissociation of a diatomic molecule which is formally equivalent to our new derivation of the self-consistent theory. Some of the material in this section is then used to derive a new steady-state approximation in Section IV.

II. Self-consistent Theory

A. Derivation

The ultimate aim of any theory of chemical kinetics is to calculate the kinetic rate constants from a knowledge of certain microscopic properties of the reactants and products. As far as recombination-dissociation kinetics is concerned, this purpose can be achieved by studying the recombination or dissociation of an ensemble of atoms and molecules which are immersed in a large excess of a chemically inert gas, M, which serves as a constant temperature heat bath throughout the reaction. From a macroscopic point of view, the rate of reaction is determined by measuring the concentration of atoms or molecules as a function of time and fitting the results to a phenomenological equation of the form

$$\mathrm{d}[X_2]/\mathrm{d}t = K\,R[M]\,[X]^2 - K\,D[M]\,[X_2]. \quad \text{(II.1)}$$

From a microscopic viewpoint, this process can best be described by the following master equation, which takes account of the concentration of vibrationally excited molecules with internal energy E_n:

$$\begin{aligned}\mathrm{d}[X_2{}^n]/\mathrm{d}t &= k\,r_n[M]\,[X]^2 - k\,d_n[M]\,[X_2{}^n]\\ &\quad + [M]\sum_{i\neq n} k_{n,i}[X_2{}^i] - [M]\sum_{j\neq n} k_{j,n}[X_2{}^n]. \quad \text{(II.2)}\end{aligned}$$

The first term represents the direct population of level n by recombination, i. e., $X + X + M \rightarrow X_2 + M$; the second term represents the opposite process. The third and fourth terms acount for transitions among he vaorius inernal degrees of freedom of the diatomic molecule.

Since our aim is to derive an equation that describes how a reacting system evolves on the macroscopic level, we will solve Eq. (II.2) by using a perturbation procedure analogous to the Hilbert and Chapman-Enskog methods for solving the Boltzmann equation [9]. In doing this, we are taking advantage of the fact that a much longer time is usually required for a reacting system to approach equilibrium on the macroscopic level than on the atomic level. This does not necessarily mean that our system is near chemical equilibrium. We shall look for a solution such that the time dependence of each of the concentrations, $[X_2{}^n(t)]$, can be expressed in terms of macroscopic variables, such as the total atomic and molecular concentrations, and the velocity of reaction. One way of actually finding such solutions is to assume that they are of the form

$$[X_2{}^n(t)] = \gamma_n[X_2(t)] + v\,f_n\,\gamma_n + \dots \quad \text{(II.3)}$$

where $\gamma_n = \exp(-E_n/k\,T) / \sum_{m=0}^{\infty} \exp(-E_n/k\,T)$

and $v = \Sigma\,\mathrm{d}[X_2{}^n]/\mathrm{d}t$, is the velocity of reaction. The first term in our expansion guarantees that our velocity of reaction is the rate at which the number of molecules with a Maxwell-Boltzmann distribution changes; this is a good approximation over macroscopic intervals of time. We are not, however, assuming that there is little or no difference between our distribution function and the Boltzmann distribution. At this point in the calculation, a problem arises because the rate of reaction, v, is one of the things we are trying to calculate. This problem can be avoided by arbitrarily limiting the expansion to a fixed number of terms, and solving the resulting equations in a self-consistent manner.

By limiting our calculation to one term, we effectively assume that

$$[X_2{}^n(t)] = \gamma_n[X_2(t)] + v(t)\,\gamma_n\,f_n \quad \text{(II.4a)}$$

to first order; it immediately follows that

$$\mathrm{d}[X_2{}^n]/\mathrm{d}t = \gamma_n\,v(t). \quad \text{(II.4b)}$$

After substituting Eq. (II.4) into Eq. (II.1), one finds

$$\begin{aligned} v &= \Big(\sum_n k\,r_n\Big)[X]^2 - \Big(\sum_n \gamma_n\,k\,d_n\Big)[X_2]\\ &\qquad - \Big([M]\sum_n k\,d_n\,\gamma_n\,f_n\Big)v \quad \text{(II.5a)}\\ &= v_0 - \Big(\sum_n k\,d_n\,\gamma_n\,f_n\Big)v \quad \text{(II.5b)}\\ &= H(T)\;v_0 \quad \text{(II.5c)}\end{aligned}$$

$$\text{where } H(T) = \Big[1 + [M]\sum_n k\,d_n\,\gamma_n\,f_n\Big]^{-1}, \quad \text{(II.5d)}$$

and v_0 is the equilibrium velocity of reaction, i. e., the value of the rate of reaction if the internal degrees of freedom could instantaneously relax to a Maxwell-Boltzmann distribution.

The value of $H(T)$ can be determined in terms of the f_n, by making the substitutions

$$[X_2^n(t)] = \gamma_n [X_2(t)] + H(T)\, v_0\, \gamma_n f_n\,, \qquad \text{(II.6a)}$$

$$\mathrm{d}[X_2^n]/\mathrm{d}t = \gamma_n H(T)\, v_0 \qquad \text{(II.6b)}$$

into our original master equation, Eq. (II.1). Doing this and making use of the principle of detailed balance, i. e., $k_{j,n}\gamma_n = k_{n,j}\gamma_j$, our original set of coupled differential equations can be reduced to the following set of simultaneous equations:

$$\gamma_n H(T) = \alpha_n - [M]\, k\, d_n (\gamma_n f_n)\, H(T) + [M]\, H(T) \Big\{ \sum_{i \neq n} k_{n,i} f_i \gamma_i - \sum_{j \neq n} k_{j,n} \gamma_n f_n \Big\} \qquad \text{(II.7)}$$

subject to the constraint, $\sum_n \gamma_n f_n = 0$. In deriving this equation, we have used the identity [11],

$$[M][X]^2 k\, r_n - [M][X_2]\, \gamma_n k\, d_n = \gamma_n k\, d_n \Big(\sum_i \gamma_i k\, d_i \Big)^{-1} v_0 \qquad \text{(II.8a)}$$

$$= \alpha_n v_0\,. \qquad \text{(II.8b)}$$

$H(T)$ is the ratio of the mean first passage time of some unit concentration of molecules whose initial distribution is $[X_2^n(0)] = \alpha_n$, T_α, to the mean first passage time of an equal number of molecules which initially have a Maxwell-Boltzmann or equilibrium distribution, i. e., $[X_2^n(0)] = \gamma_n$, T_{mb} [12]. The first step in arriving at this conclusion is to realize that the set of simultaneous equations one must solve to calculate the mean first passage time of a given number of molecules which initially have the distribution, T_α, is

$$\alpha_n = -[M]\, k\, d_n (\gamma_n g_n) + [M] \Big\{ \sum_{i \neq n} k_{n,i}\, g_i \gamma_i - \sum_{i \neq n} \gamma_n k_{j,n}\, g_n \Big\}. \qquad \text{(II.9)}$$

The equation needed to calculate T_{mb} can be obtained by replacing the α_n appearing on the left-hand side of Eq. (II.9) by γ_n. The mean first passage time, itself, is equal to $-\sum_n \gamma_n g_n$. The constraint, $\sum_n \gamma_n f_n = 0$, appearing in Eq. (II.7), forces the $H(T)$ to be a ratio of mean first passage times; one way to see this is to divide each of the terms in Eq. (II.7) by $H(T)$.

By an interesting coincidence, $H(T)$ is also the ratio of the equilibrium dissociation time, the time required to dissociate a given number of molecules which always maintain a Maxwell-Boltzmann distribution throughout the reaction, T_{eq}, to the mean first passage time of the same number of molecules which initially have a Maxwell-Boltzmann distribution, T_{mb}, because $T_\alpha = T_{\mathrm{eq}}$. In order to calculate T_α, one must solve Eq. (II.9). Since the relaxation rate constants obey the principle of detailed balance, i. e., $k_{n,i}\gamma_i = k_{j,n}\gamma_n$, the solution of these equations is

$$g_n = -1/K D_{\mathrm{eq}} \qquad \text{(II.10a)}$$

where

$$K D_{\mathrm{eq}} = [M] \sum_{n=0}^{N} \gamma_n k\, d_n \qquad \text{(II.10b)}$$

is the equilibrium dissociation rate constant, i. e., the rate constant for dissociating a diatomic molecule whose internal degrees of freedom maintain a Maxwell-Boltzmann distribution throughout the reaction; thus,

$$T_\alpha = \sum (\gamma_n / K D_{\mathrm{eq}}) = 1/K D_{\mathrm{eq}} = T_{\mathrm{eq}}\,. \qquad \text{(II.10c)}$$

Even though this theory predicts that the approach to equilibrium can be described by the classical phenomenological equation, (II.1), there are some obvious limitations on the validity of our theory. For instance, our expression for the dissociation rate constant is equal to the mean first passage time for some unit concentration of molecules which initially have a Boltzmann distribution. This result is probably very accurate for a reacting system very far from chemical equilibrium; it becomes less meaningful as we approach equilibrium. This difficulty can be bypassed by extending the theory to higher order. Before we look into this difficult problem, we are going to try to gain some insights as to what makes a theory like this work by investigating some of the theory's physical implications, and seeing what happens when we use it to solve a nontrivial problem for which an exact solution exists.

B. Physical Implications of Self-consistent Theory

The concept of a vibrational relaxation time plays a very important role in almost any discussion about the importance of nonequilibrium effects in recombination-dissociation kinetics. Since there is no unique definition of a vibrational relaxation time, T_{r}, we will have to investigate some of the physical implications of our theory to evaluate it. As far as dissociation reactions are concerned, a reasonable definition is

$$T_{\mathrm{r}} = T_{\mathrm{mb}} - T_{\mathrm{eq}}\,. \qquad \text{(II.11)}$$

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[11] This equation is derived in Appendix A of Ref. [10].

[12] E. W. Montroll and K. E. Shuler, Advan. Chem. Phys. **1**, 361 [1958].

Starting with Eq. (II.5), it is easy to show that

$$H(T)=\frac{\left(\sum\limits_{n}\gamma_n k\, d_n\right)^{-1}}{\left(\sum\limits_{n}\gamma_n k\, d_n\right)^{-1}+\sum\limits_{n}\alpha_n f_n}=\frac{T_{\mathrm{mb}}}{T_{\mathrm{eq}}} \qquad \text{(II.12a)}$$

where the value of α_n is defined by Eq. (II.8). Since $(\sum_n \gamma_n k\, d_n)^{-1}$ is the equilibrium dissociation time, $T_{\mathrm{r}}=\sum_n \alpha_n f_n$, and $T_{\mathrm{r}}/T_{\mathrm{eq}}=\sum_n \gamma_n f_n k\, d_n$. As far as dissociation reactions are concerned, this is the ratio we are seeking; it also plays an important role in atomic recombination kinetics.

Since evaluating $H(T)$ allows us to obtain the f_n, it is easy to show how solving Eq. (II.7) is also equivalent to studying how a highly excited molecule relaxes to a Boltzmann distribution. Instead of using Eq. (II.8) as the basis for converting our original set of differential equations into a set of simultaneous equations, we will use the following identity:

$$[\mathrm{M}]\,[\mathrm{X}]^2\, k\, r_n-[\mathrm{M}]\,[\mathrm{X}_2]\,\gamma_n k\, d_n - \gamma_n k\, d_n[\mathrm{M}]\, f_n H(T)\, v_0=\boldsymbol{\beta_n H(T)\, v_0} \qquad \text{(II.13)}$$

where
$$\beta_n=\frac{\alpha_n-\gamma_n k\, d_n[\mathrm{M}]\, f_n \mathrm{H}(T)}{H(T)}. \qquad \text{(II.14)}$$

Instead of Eq. (II.7), we now have

$$\gamma_n=\beta_n+[\mathrm{M}]\left\{\sum_{i\neq n} k_{n,i} f_i \gamma_i-\sum_{j\neq n} k_{j,n} f_n \gamma_n\right\}. \qquad \text{(II.15)}$$

In Appendix B of I (Ref. [10]), we have encountered equations similar to these in studying how a highly excited molecule relaxes to a Maxwell-Boltzmann distribution, $[\mathrm{X}_2{}^m(\infty)]=\gamma_n$, from the initial distribution $[\mathrm{X}_2{}^n(0)]=\beta_n$. The $\gamma_n f_n$ can be thought of as being the average time required for each individual level to relax to its equilibrium value. In the cascade model of atomic recombination reactions, two atoms recombine in the presence f a third body, resulting in the formation of a highly excited molecule. Since we are usually interested in the formation of molecules with no internal excitation, a recombination is not considered to have occurred, unless the excited species is deactivated before it is redissociated. As we have already seen, the time required for deactivation is $\gamma_n f_n$; the corresponding time for redissociation is $1/k\, d_n$. In a recombining gas, pairs of atoms will continue to recombine into a given molecular level until thatl evel reaches equilibrium with respect to the atomic gas; i. e.

$$k\, r_n[\mathrm{X}]^2-k\, d_n[\mathrm{X}_2{}^n]=0\,.$$

Thus, $1/k\, d_n$ can be regarded as the chemical relaxation time, and $\gamma_n f_m k\, d_n$ as the ratio of the vibrational and chemical relaxation times for the n-th level. The summation, $\Sigma_1 \gamma_n f_n k\, d_n$, is the sum of all such ratios and can also be regarded as the ratio of the vibrational and chemical relaxation times for the recombination reaction.

Our derivation of the selfconsistent theory is based on certain mathematical techniques for solving the Boltzmann equation. If we had been clever enough to independently derive the concepts of vibrational relaxation mentioned in the previous paragraphs, we could have derived our theory without using this formalism. Suppose we let $v-v_0$ denote the difference between the actual velocity and the equilibrium velocity, the rate of reaction if the molecular internal degrees of freedom were able to maintain a Boltzmann distribution. As far as dissociation reactions are concerned, this difference has its origin in the depletion of the population of certain reactioe levels with respect to their equilibrium value. If T_{r} is the relaxation time for these levels, then $v\, T_{\mathrm{r}}$ is the amount of this depletion at any instant of time. Under equilibrium conditions, these molecules would make a contribution of $v\, T_{\mathrm{r}}/T_{\mathrm{eq}}$ to the overall rate of dissociation, where T_{eq} is the reciprocal of the equilibrium dissociation rate constant. Therefore, $v_0-v=v\, T_{\mathrm{r}}/T_{\mathrm{eq}}$. The analysis of recombination kinetics is somewhat different, even though it has its origin in the finite time required for the deactivation of the excted molecules formed by recombination. Every molecule that eventually recombines spends a certatin amount of time in each of the excited vibrational states. Because it is energetically more favourable for the highly excited states to be at equilibrium with respect to the atomic gas, i. e., $k\, r_n[\mathrm{X}]^2-k\, d_n[\mathrm{X}_2{}^n]=0$, the rate of recombination is controlled by the rate of deactivation of these molecules. Every excited molecule destined to recombine, i. e., relax to a Boltzmann distribution, is preventing other pairs of atoms from *immediately* recombining into these levels. Since each of the v molecules per second that recombine spends $\gamma_n f_n$ seconds on each level, there are $v\,\gamma_n f_n$ extra molecules on these levels; they prevent $v\,\gamma_n f_n$ molecules from recombining into each level. Thus, $v_0-v=v\sum_n \gamma_n f_n k\, d_n$. The uniqueness of the selfconsistent theory rests on the identity of our two expressions for v_0-v.

While these models of a reacting system do not guarantee the validity of our theory, they do provide some clues as to why our approach works and ques for solving systems of differential equations how to improve it. The philosophy behind the selfconsistent theory is analogous to averaging techniques for solving systems of differential equation [13–15]. It is often possible to describe the evolution of the slow component of a nonlinear electrical or mechanical oscillator in terms of the average behavior of its more rapid motion. Looking back, we now see how we have been trying to describe the slow macroscopic evolution of a reacting system in terms of its time-averaged microscopic behavior. This began when we tried to desribe the time dependence of the macroscopic motion in terms of the macroscopic rate of reaction. A better description of the approach to equilibrium can be obtained by using a more sophisticated method of averaging that accounts for slow change in the velocity of reaction at any given instant. In the next section, we shall gain some insights as to how to extend the selfconsistent theory to higher order by investigating a solvable model of a dissociating diatomic molecule.

III. Dissociation of a Diatomic Molecule

A. Time Independent Theory

Almost all of the nonequilibrium theories of chemical kinetics are based on the same principle as the Chapman-Enskog method for solving the Boltzmann equation. These theories attempt to predict how a reacting system approaches thermydynamic equilibrium over macroscopic intervals of time, once the transient behavior has vanished. One way of illustrating the mathematical and physical significance of this type of solution is to analyze a model for which we have an exact solution. A number of interesting things have been learned about the importance of nonequilibrium effects in dissociation kinetics from an analysis of the model whose master equation is:

$$\mathrm{d}[X_2{}^n]/\mathrm{d}t = -k\,d[M]\,[X_2{}^n] + \sum_{m \neq n} [M]\,k_{n,m}[X_2{}^m] - \sum_{m \neq n} [M]\,k_{m,n}[X_2{}^n]. \qquad \text{(III.1)}$$

Since the transition probabilities satisfy the principle of detailed belance,

$$k_{m,n} \exp(-E_n/k\,T) = k_{n,m} \exp(-E_m/k\,T). \qquad \text{(III.2)}$$

Making the substitution

$$Y_n = [X_2{}^n] \exp(E_n/2\,k\,T) \qquad \text{(III.3)}$$

enables us to work with the more symmetric equation

$$\frac{\mathrm{d}Y_n}{\mathrm{d}t} = \sum_{m \neq n} Y_m\,k_{n,m} \exp[(E_n - E_m)/2\,k\,T] - Y_n \sum_{m \neq n} k_{m,n} - k\,d_n\,Y_n \qquad \text{(III.4a)}$$

$$= \sum_m A_{nm}\,Y_m\,. \qquad \text{(III.4b)}$$

The solution of Eq. (III.1) is

$$[X_2(t)] = \exp(-E_n/2\,k\,T) \sum_m d_m \exp(\lambda_m\,t), \qquad \text{(III.5)}$$

where the coefficients d_m depend on the initial state of the system, and the are the eigenvalues of the symmetric matrix, A [12].

Since the chemical kineticist tries to describe the dissociation of a diatomic molecule by the phenomenological equation

$$\mathrm{d}[X_2]/\mathrm{d}t = -K\,D[X_2] \qquad \text{(III.6)}$$

one usually equates $K\,D$ to the eigenvalue of A with the lowest absolute value, λ_0. Since all of the $\lambda_m < 0$, this procedure is equivalent to retaining one term of the exact solution to the problem. If $|\lambda_m| \gg \lambda_0$, this corresponds to the asymptotic solution to our problem and represents the approach to equilibrium on the macroscopic time scale. We can learn something about the importance of nonequilibrium effects in dissociation kinetics by using perturbation theory to calculate λ_0.

By setting all of the $k\,d_n$ equal to zero, Eq. (III.4) reduces to the following equation for the relaxation of a nonequilibrium distribution:

$$\mathrm{d}y/\mathrm{d}t = R\,y \qquad \text{(III.7)}$$

where $R_{nm} = \exp[(E_n - E_m)/2\,k\,T]\;k_{n,m}\,, \qquad \text{(III.8a)}$

$$R_{nn} = -\sum_{m \neq n} k_{m,n}\,. \qquad \text{(III.8b)}$$

Since there is no mechanism for dissociation, the largest eigenvalue is $\lambda_0 = 0$, and the corresponding

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[13] R. Bellman and J. M. Richardson, Proc. Nat. Acad. Sci. U.S. **47**, 1191 [1961].

[14] P. Goldberg and G. Sandri, Phys. Rev. **154**, 188, 199 [1967]. Compare Eq. (13) of Ref. [8] with Goldberg and Sandri's Eq. (1.12) on page 190.

[15] V. M. Volosov, Russian Mathematical Surveys **17**, 1 [1962].

eigenvector is

$$\mathbf{V}_n{}^0 = \exp(-E_n/2\,k\,T) \Big/ \Big(\sum_m \exp(-E_m/k\,T)\Big)^{1/2} = \gamma_n{}^{1/2}. \qquad \text{(III.9a, b)}$$

This can be verified by direct substitution. If $K\,D$ is the matrix whose only nonzero elements are $K\,D_{nn} = k\,d$, the first order correction to $\lambda c = 0$ is

$$\lambda_0{}' = -\mathbf{V}_0 \cdot K\,D\,\mathbf{V}_0 = -\sum_n \gamma_n\,k\,d_n \qquad \text{(III.10a, b)}$$

γ_n being defined by Eq. (III.9a). This correction is the negative of the equilibrium dissociation constant, because the equilibrium distribution of the relaxation problem, $\mathbf{V}_0$, is related to a Maxwell-Boltzmann distribution. We have to go to higher order perturbation theory if we want to calculate the departure of the reaction from its equilibrium velocity.

Our first impulse is to use the conventional approach to perturbation theory to calculate the second and higher order correction to λ_0. This approach requires a detailed knowledge of all of the eigenvalues and eigenvector of R. For instance, the second order correction to λ_0 is

$$\lambda_0{}^2 = \sum_{n \neq 0} \frac{(\mathbf{V}_0 \cdot K\,D\,\mathbf{V}_n)\,(\mathbf{V}_n \cdot K\,D\,\mathbf{V}_0)}{\lambda_0 - \lambda_n} \qquad \text{(III.11)}$$

where the $\mathbf{V}_n$ and λ_n are the eigenvectors and eigenvalues of R[12]. Since we only have a detailed knowledge of λ_0 and $\mathbf{V}_0$, we will evaluate this summation by a method widely used in the quantum theory of electric and magnetic interactions in molecules[16]. Suppose we define the vector $\boldsymbol{U}^1$ as being the solution of the matrixvector equation:

$$(\lambda_0 - R)\,\boldsymbol{U}^1 = -K\,D\,\mathbf{V}_0 + (\mathbf{V}_0 \cdot K\,D\,\mathbf{V}_0)\,\mathbf{V}_0\,. \qquad \text{(III.12)}$$

Once we have the solution for this equation, our summation can be evaluated by noting

$$\lambda_0{}^2 = -\sum_{n \neq 0} \frac{(\mathbf{V}_0 \cdot K\,D\,\mathbf{V}_n)\,(\mathbf{V}_n \cdot [(\lambda_0 - R)]\,\boldsymbol{U}^1)}{\lambda_0 - \lambda_n} \qquad \text{(III.13a)}$$

$$= -\sum_{n \neq 0} (\mathbf{V}_0 \cdot K\,D\,\mathbf{V}_n)\,(\mathbf{V}_n \cdot \boldsymbol{U}^1) \qquad \text{(III.13b)}$$

$$= -\mathbf{V}_0 \cdot K\,D\,\boldsymbol{U}_1 + (\mathbf{V}_0 \cdot K\,D\,\mathbf{V}_0)\,(\mathbf{V}_0 \cdot \boldsymbol{U}^1). \qquad \text{(III.13c)}$$

Equation (III.13a) results from substituting the expression for $-K\,D\,\mathbf{V}_0$ in Eq. (III.12) into Eq. (III.11) and recalling that $\mathbf{V}_0 \cdot \mathbf{V}_n = 0$. Since R is a symmetric matrix, it is self-adjoint; therefore, Eq. (III.13b) can be obtained from the following equations:

$$(v_n \cdot [\lambda_0 - R]\,\boldsymbol{U}^1) = [(\lambda_0 - R)\,\mathbf{V}_n \cdot \boldsymbol{U}^1] \qquad \text{(III.14a)}$$

$$= (\lambda_0 - \lambda_n)\,\mathbf{V}_n \cdot \boldsymbol{U}^1. \qquad \text{(III.14b)}$$

Equation (III.13c) is a consequence of the completeness relationship, i. e.,

$$\boldsymbol{U}_1 = \sum_{n=0}^{N} (\mathbf{V}_n \cdot \boldsymbol{U}_1)\,\mathbf{V}_n\,, \qquad \text{(III.15a)}$$

$$K\,D\,\boldsymbol{U}_1 = \sum_{n=0}^{N} (\mathbf{V}_n \cdot \boldsymbol{U}_1)\,K\,D\,\mathbf{V}_n\,, \qquad \text{(III.15b)}$$

$$\mathbf{V}_0 \cdot K\,D\,\boldsymbol{U}_1 = \sum (\mathbf{V}_n \cdot \boldsymbol{U}_1)\,(\mathbf{V}_0 \cdot K\,D\,\mathbf{V}_n)\,. \qquad \text{(III.15c)}$$

Thus, we can evaluate $\lambda_0{}^2$ from Eq. (III.13c), which only requires a knowledge of $\mathbf{V}_0$ and $\boldsymbol{U}_1$. If we were to use the method of Pyun and Ross to solve Eq. (III.1), we would have to solve an equation equivalent to (III.12)[9]. Their constraint for guaranteeing conservation of the total number of molecules is equivalent to requiring that $\boldsymbol{U}_1$ be orthogonal to $\mathbf{V}_0$; thus,

$$\lambda_0{}^2 = -(\mathbf{V}_0 \cdot K\,D\,\boldsymbol{U}_1)\,. \qquad \text{(III.16a)}$$

This is equivalent to their expression

$$\lambda_0{}^2 = -\sum_n k\,d_n\,\gamma_n\,g_n \qquad \text{(III.16b)}$$

where $\sum_n \gamma_n\,g_n = 0$, is their orthogonality constraint.

In order to rederive our selfconsistent theory, we have to use the matrixvector analogue of the resolvent operator formulation of stationary state perturbation theory[17]. In trying to solve the eigenvalue problem

$$(R - K\,D - \lambda_0)\,\mathbf{V} = 0 \qquad \text{(III.17)}$$

it is convenient to introduce the resolvent operator

$$R\,S(Z) = (Z\,I - R + K\,D)^{-1} \qquad \text{(III.18)}$$

and rewrite Eq. (III.17) as

$$(\lambda_0 - R + K\,D)\,\mathbf{V}\,\mathbf{P} = (-K\,D - \Delta\lambda I)\,\mathbf{V}_0 \qquad \text{(III.19)}$$

where $\lambda_0 = \lambda_0{}^0 + \Delta\lambda$ and I is the unit matrix. The formal solution of Eq. (III.18) is

$$\mathbf{V}\,\mathbf{P} = R\,S(\lambda_0)\,(-K\,D - \Delta\lambda\,I)\,\mathbf{V}_0\,. \qquad \text{(III.20)}$$

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[16] J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Advan. Quantum Chemistry I [1964].

[17] R. Yaris, J. Chem. Phys. **40**, 1891 [1964].

Since part of our job is to calculate λ_0 and $\Delta\lambda$, we have to use the identity

$$(A-C)^{-1}=A^{-1}+(A-C)^{-1}C\,A^{-1} \qquad \text{(III.21)}$$

to expand $R\,S(\lambda_0)$. If we were to let $A=(\lambda_0{}^0-R)$ and $C=(-K\,D-\Delta\lambda)$, we would find, to first order, that

$$\mathbf{V}\,\mathbf{P}=(\lambda_0{}^0-R)^1\,(-K\,D-(\Delta\lambda)^1\,I)\,\mathbf{V}_0\,. \qquad \text{(III.22)}$$

As soon as we recall that, for our problem, $\lambda_0{}^0=0$ and $(\Delta\lambda)^1=-\mathbf{V}_0\cdot K\,D\,\mathbf{V}_0$, we will realize the equivalence of Eq. (III.22) and Eq. (III.12).

In order to use the resolvent formalism to derive the analogue of the selfconsistent theory, we have only to let $A=(\lambda_0{}^0+K\,D-R)$ and $C=-\Delta\lambda\,I$. With this new choice and again expanding $\mathbf{V}\,\mathbf{P}$ and $\Delta\lambda$, our first order equation is now

$$(K\,D-R)\,\mathbf{P}_1=(-K\,D-\Delta\lambda_1\,I)\,\mathbf{V}_0; \qquad \text{(III.23a)}$$

this implies that

$$\begin{aligned}\Delta\lambda_1&=-\mathbf{V}_0\cdot K\,D\,\mathbf{V}_0+\mathbf{V}_0\cdot(-K\,D+R)\,\mathbf{P}_1 && \text{(III.23b)}\\ &=-\mathbf{V}_0\cdot K\,D\,\mathbf{V}_0-\mathbf{V}_0\cdot K\,D\,\mathbf{P}_1\,. && \text{(III.23c)}\end{aligned}$$

The last equation is a consequence of $R\,\mathbf{V}_0=0$. It is relatively easy to show that these equations are equivalent to the ones we have in the selfconsistent theory, Eq. (II.6), if we require $\mathbf{P}_1$ to be proportional to $\Delta\lambda_1$. Our requirement that $\Sigma\,\gamma_n\,f_n=0$ is equivalent to having $\mathbf{V}_0\cdot\mathbf{V}\,\mathbf{P}_1=0$; this orthogonality will play an important role in providing a more rigorous mathematical basis for our theory.

B. Time-Dependent Theory

In addition to providing us with some valuable insights about our own work and the theories of Ross and Mazur and Pyun and Ross, our model of a dissociating diatomic molecule can also provide some valuable insights about the higher order corrections to these theories. In order to obtain this information, we will write our master equation as

$$\mathrm{d}\mathbf{Y}/\mathrm{d}t=(R-K\,D)\,\mathbf{Y}\,, \qquad \text{(III.24)}$$

where the definition of the matrices R and $K\,D$ can be found in the discusion following Eq. (III.7) and Eq. (III.9), respectively. Introducing the new variable,

$$\mathbf{Z}=\exp(-R\,t)\,\mathbf{Y}\,, \qquad \text{(III.25a)}$$

Eq. (III.24) becomes

$$\mathrm{d}\mathbf{Z}/\mathrm{d}t=-\exp(-R\,t)\,K\,D\exp(+R\,t)\,\mathbf{Z}. \qquad \text{(III.25b)}$$

We will look for a solution of the form

$$\mathbf{Z}=\mathbf{Z}_0+\mathbf{Z}_1+\mathbf{Z}_2+\ldots\mathbf{Z}_n \qquad \text{(III.26a)}$$

where $$\mathbf{Z}_0=\exp(-R\,t)\,\boldsymbol{\gamma}^{1/2}=\boldsymbol{\gamma}^{1/2}. \qquad \text{(III.26b)}$$

Substituting Eq. (III.26) into (III.25b) yields the first order result

$$\begin{aligned}\mathrm{d}\mathbf{Z}_1/\mathrm{d}t&=\exp(-R\,t)\,K\,D\,\boldsymbol{\gamma}^{1/2} && \text{(III.27a)}\\ &=-\sum\exp(-\lambda_m\,t)\,(\mathbf{V}_n\cdot K\,D\,\boldsymbol{\gamma}^{1/2})\,\mathbf{V}_n\\ &\quad-(\boldsymbol{\gamma}^{1/2}\cdot K\,D\boldsymbol{\gamma}^{1/2})\,\boldsymbol{\gamma}^{1/2}. && \text{(III.27b)}\end{aligned}$$

The λ_n and $\mathbf{V}_n$ are the eigenvalues and eigenvectors of R; λ_0 and v_0 are zero and $\boldsymbol{\gamma}^{1/2}$, respectively. Integrating Eq. (III.27), we find

$$\begin{aligned}\mathbf{Y}(t)=\sum_n(\mathbf{V}_n\cdot K\,D\,\boldsymbol{\gamma}^{1/2})\,\mathbf{V}_n/\lambda_n && \text{(III.28)}\\ -t(\boldsymbol{\gamma}^{1/2}\cdot K\,D\,\boldsymbol{\gamma}^{1/2})\,\boldsymbol{\gamma}^{1/2}+\text{const}\,.\end{aligned}$$

Since $\mathbf{Y}(0)=\boldsymbol{\gamma}^{1/2}$,

$$\begin{aligned}\mathbf{Y}(t)&=\boldsymbol{\gamma}^{1/2}[1-t(\boldsymbol{\gamma}^{1/2}\cdot K\,D\,\boldsymbol{\gamma}^{1/2})] && \text{(III.29a)}\\ &=\boldsymbol{\gamma}^{1/2}[1-t\sum_n\gamma_n\,k\,d_n]\,. && \text{(III.29b)}\end{aligned}$$

This solution is only valid over short intervals of time such that $t\ll(\sum\limits_n\gamma_n\,k\,d_n)^{-1}$; over long periods of time it diverges. This is a well-known problem in the study of nonlinear electrical and mechanical systems, and there are a number of techniques for solving it. Some of these techniques have already found their way into statistical mechanics. The original work of Ross and Mazur contains an expansion of the time derivative that is analogous to the method of multiple time scales [14]. Our problem is more easily solved by using Bogolyubov's method of averaging [15]. We shall seek a change of variables of the form

$$\mathbf{Z}=U_0(\mathbf{X}\,\mathbf{P})+\sum_{n=1}U_n(\mathbf{X}\,\mathbf{P},t)\,. \qquad \text{(III.30)}$$

The new set of functions $X\,P_n(t)$ are chosen such that Eq. (III.25b) becomes

$$\mathrm{d}\mathbf{X}\,\mathbf{P}/\mathrm{d}t=D_n(\mathbf{X}\,\mathbf{P})\,. \qquad \text{(III.31a)}$$

The time variable *does not appear explicitly* in this equation. If $K\,D=0$, we shall require the $\boldsymbol{U}_n$ and D_n $(n\geqq 1)$ to vanish; therefore, $\boldsymbol{U}_0=\mathbf{X}\,\mathbf{P}=a(t)\;{}^{1/2}$. To evaluate the functions D_n and U_n we have to use Eq. (III.30) and Eq. (III.31a) to derive the following expression:

$$\begin{aligned}\frac{\mathrm{d}\mathbf{Z}}{\mathrm{d}t}&=D_1(\mathbf{X}\,\mathbf{P})+\frac{\partial U_1(\mathbf{X}\,\mathbf{P},t)}{\partial t}+D_2(\mathbf{X}\,\mathbf{P})\\ &\quad+\frac{D_1(\mathbf{X}\,\mathbf{P})\,\partial U_1(\mathbf{X}\,\mathbf{P},t)}{\partial\mathbf{X}\,\mathbf{P}}+\frac{\partial U_2(\mathbf{X}\,\mathbf{P},t)}{\partial t}+\cdots\,. && \text{(III.31b)}\end{aligned}$$

Substituting this eqution into Eq. (III.25b), we find

$$D_1(\boldsymbol{X}\boldsymbol{P}) = -a(t)\,(\boldsymbol{\gamma}^{1/2}\cdot K D\boldsymbol{\gamma}^{1/2})\,\boldsymbol{\gamma}^{1/2}, \tag{III.32a}$$

$$U_1(\boldsymbol{X}\boldsymbol{P}, t) \tag{III.32b}$$
$$= a(t)\sum_{n=0}\exp(-\lambda_n t)\,(\mathbf{V}_n\cdot K D\boldsymbol{\gamma}^{1/2})\,\mathbf{V}_n/\lambda_n,$$

$$D_2(\boldsymbol{X}\boldsymbol{P} = \tag{III.32c}$$
$$-a(t)\sum_{n=0}(\boldsymbol{\gamma}^{1/2}\cdot K D\mathbf{V}_n)\,(\mathbf{V}_n\cdot K D\boldsymbol{\gamma}^{1/2})\,\boldsymbol{\gamma}^{1/2}/\lambda_n.$$

The equivalence of the two summations appearing in Eq. (III.11) and Eq. (III.32c) plus the discussion following Eq. (III.15) suggests that our analysis is a special case of the theory of Pyun and Ross. This dynamic analysis also emphasizes two very interesting features of this type of theory. In going from Eq. (III.25b) to Eq. (III.31), we have implicitly dediced to confine our interest to how the number of molecules with a Boltzmann distribution changes per unit time. Our neglect of the constants of integration in Eq. (III.32) is equivalent to ignoring the transient behavior of our system and giving our full attention to its asymptotic or macroscopic motion.

The transformation used to derive the results equivalent to the work of Pyun and Ross, Eq. (IIII.25a), is equivalent to seeking a solution to Eq. (III.24) of the form

$$\mathbf{Y}(t) = a_0(t)\,\boldsymbol{\gamma}^{1/2} + \sum_{n=0}a_n(t)\,\mathbf{V}_n\exp(\lambda_n t) \tag{III.33}$$

where the $\mathbf{V}_n$ and $\boldsymbol{\gamma}^{1/2}$ are the eigenvectors of R whose eigenvalues are λ_n and zero, respectively. In order to derive the result analogous to the self-consistent theory, we will look for a solution of the form

$$\mathbf{Y}(t) = b_0(t)\,\boldsymbol{\gamma}^{1/2} + \sum_{n=1}^{N}b_n(t)\,\mathbf{V}\boldsymbol{P}_n\exp(\lambda P_n t) \tag{III.34a}$$

where the $\mathbf{V}\boldsymbol{P}_n$ have the following properties:

1) $\mathbf{V}\boldsymbol{P}_n\cdot\boldsymbol{\gamma}^{1/2} = 0,$ (III.34b)

2) $\mathbf{V}\boldsymbol{P}_n\cdot\mathbf{V}\boldsymbol{P}_m = \delta_{n,m},$ (III.34c)

3) $\mathbf{V}\boldsymbol{P}_n\cdot(R-KD)\,\mathbf{V}\boldsymbol{P}_m = \lambda P_m\,\delta_{n,m}.$ (III.34d)

The $\mathbf{V}\boldsymbol{P}_n$ and $\boldsymbol{\gamma}\boldsymbol{P}_n$ can be obtained by diagonalizing the $(N-1)$ square matrix whose elements are $M_{i,j} = (\mathbf{V}_i\cdot(R-KD)\,\mathbf{V}_j)$; the $\mathbf{V}_i$ are the eigenvectors of R orthogonal to $\boldsymbol{\gamma}^{1/2}$. Using all of this information, we can easily obtain the following set of equations from Eq. (III.24):

$$\mathrm{d}b_0/\mathrm{d}t = b_0(t)\,\boldsymbol{\gamma}^{1/2}\cdot K D\,\boldsymbol{\gamma}^{1/2} \tag{III.35a}$$
$$+\sum_{n=1}^{N}b_n(t)\,\boldsymbol{\gamma}^{1/2}\,K D\,\mathbf{V}\boldsymbol{P}_n\exp(\lambda P_n t),$$

$$\mathrm{d}b_n/\mathrm{d}t = b_0(t)\,\mathbf{V}\boldsymbol{P}_n\cdot K D\boldsymbol{\gamma}^{1/2}\exp(\lambda P_n t). \tag{III.35b}$$

If we are to use the method of averaging to solve these equations, we must concentrate our attention on describing the evaluation of our system in terms of those molecules having a Maxwell-Boltzmann distribution, i. e., $b_0\boldsymbol{\gamma}^{1/2}$. To first order we have the familiar equilibrium result

$$b_0(t) = \exp(-t\sum_n\gamma_n k\,d_n). \tag{III.36a}$$

Integrating Eq. (III.35b), one finds

$$b_n = -b_0\,\mathbf{V}\boldsymbol{P}_n\cdot K D\,\boldsymbol{\gamma}^{1/2}\exp(\lambda P_n \mathrm{t})/(\lambda P_n) + \text{const}. \tag{III.36b}$$

This leads to a better solution,

$$b_0 = \exp\Big\{-t\Big[\sum_n\gamma_n k\,d_n \tag{III.36c}$$
$$+\sum_n(\boldsymbol{\gamma}^{1/2}\cdot K D\,\mathbf{V}\boldsymbol{P}_n)^2/(\lambda P_n)\Big]\Big\}.$$

Even though no iterative procedure has been used to derive the above result, it is equivalent to the self-consistent theory. In fact, we have implicitly found a noniterative method for solving Eq. (III.23a). Since $\boldsymbol{P}_1$ is orthogonal to $\boldsymbol{\gamma}^{1/2}$, it can be expanded in terms of the $\mathbf{V}\boldsymbol{P}_n$, giving

$$\boldsymbol{P}_1 = -\sum_n\langle\mathbf{V}\boldsymbol{P}_n\cdot K D\boldsymbol{\gamma}^{1/2}\rangle\,\mathbf{V}\boldsymbol{P}_n/(\lambda P_n). \tag{III.37}$$

If we let $\Delta\lambda_1 = \boldsymbol{\gamma}^{1/2}\cdot K D\boldsymbol{\gamma}^{1/2} + \boldsymbol{\gamma}^{1/2}\cdot K D\,\boldsymbol{P}_1$, Eq. (III.37) is a solution to Eq. (III.23a).

C. Physical Implications

Our original mativation for studying this model was to see how well the predictions of the selfconsistent theory compared with the exact result. This aspect of our investigation has proved to be more profitable than we expected. Some of this work will later be used to derive a more concise formulation of the selfconsistent theory. If we think of the dissociation of a diatomic molecule as a kineticist would measure it, we can also translate the mathematical differences between our work and the theories of Pyun and Rosss and Ross and Mazur into more physically meaningful terms. As far as the mathematics of the problem is concerned, the concentration of diatomic molecules decays as $\exp(\lambda P_0 t)$, no matter how λP_0 is partitioned. As far as the physics of the problem is concerned, this is not always true. In the real world, the kineticist follows the progress of a reaction by measuring the concentration of one of the reactants or products as a function of time. Because of the finite resolving power of the instrument used to perform these measurements, the concentration of the species of interest must change by some minimum amount, before the rate of reaction can be measured. The probability of obtaining a more accurate value of the rate constant improves as the measurements are extended over longer periods of time. To see how this comes about, let's suppose we are interested in the dissociation of a diatomic molecule whose dissociation rate constant is 1.001×10^{-3} per unit time. In the early stages of the reaction, it should be possible to fit a plot of concentration versus (macroscopic) time to a curve of the form, $c = \exp(-\varepsilon t)$, where $\varepsilon = 1/1000$. Over a longer period of ime such hat T is of the order of 10^6, a better fit would be $c = \exp(-\varepsilon t - \varepsilon^2 t)$. The equation

$$\mathrm{d}c/\mathrm{d}t\,|_1 = -\varepsilon c \tag{III.38a}$$

would provide a good description of how the concentration changes in the early stages of the reaction, whereas the equation

$$\mathrm{d}c/\mathrm{d}t\,|_2 = -\varepsilon^2 c \tag{III.38b}$$

tells us how the evolution of the reacting system will depart from Eq. (III.38a) over longer periods of time. This is the physical significance of Eq. (III.31a) and Eq. (13) of reference [8], if $\varepsilon \ll 1$.

In terms of acquiring more information, making measurements over longer periods of time is equivalent to extending a perturbation calculation to higher order. If we were to calculate λP_0 by perturbation theory, we might find that the first order correction or equilibrium dissociation constant is 1.0×10^{-3} and the second order correction approximately 1.0×10^{-6}. The kineticist may be completely ignorant of perturbation theory, but the macroscopic nature of his measurements is analogous to the method of averaging. These measurements only yield information about the average behavior of the rapid microscopic motion of the system over certain periods of time. The only way of acquiring additional information is to make more accurate measurements or to follow the evolution of the reacting system over longer periods of time so that the concentration changes due to higher order effects become large enough to be measured. This relation between the measuring process and perturbation theory is one way of accounting for some of the differences between our work and the theory of Ross and Mazur.

In I (Ref. [10]), we were able to show that the self-consistent theory accounts for the fact that not only does the reaction perturb the equilibrium distribution of the internal degrees of freedom, but the perturbed distribution eventually slows down the rate of reaction in order to minimize the perturbation of the internal degrees of freedom. This is the vibrational analogue of Le Chatelier's principle. The same type of argument can be applied to our model of a dissociating diatomic molecule. In using the method of averaging to analyze this model, we found it convenient to introduce two sets of vectors. The vector $\boldsymbol{\gamma}^{1/2}$ of Eq. (III.33) is present in both sets to enable us to keep track of those molecules having a Maxwell-Boltzmann distribution. The other members of the first set are the eigenvectors of the relaxation matrix R of Eq. (III.33). These vectors yield results equivalent to the theory of Ross et al. They should provide a convenient basis for expansion, when the rate of relaxation is almost instantaneous compared to the rate of dissociation, i. e., there is almost no difference between the equilibrium dissociation time and the mean firt passage time for some unit concentration of molecules which initially have an equilibrium distribution. This situation arises when the dissociation rate constants, $K d_n$, are much smaller than the rate constants for vibrational relaxation, and the rate of dissociation is governed by the $K d_n$ [3]. There has recently been a great deal of interest in dissociation reactions that are governed by the rate of relaxation [18, 19]. Under these conditions, the distribution between the rate of relaxation and the rate of reaction disappears. This disappearance is reflected in the vectors $\boldsymbol{V} \boldsymbol{P}_n$ of Eq. (III.34). These vectors are eigenvectors of the operator

$$W = Q(R - K D)\, Q\,,$$

where $Q = I - P$ and I is the unit matrix or operator and the projection operator, P, satisfies the equation

$$P\,\mathbf{V} = (\boldsymbol{\gamma}^{1/2} \cdot \mathbf{V})\,\boldsymbol{\gamma}^{1/2}. \tag{III.39}$$

Our formula for W and Eq. (III.34) indicates that the relaxation, R, and reaction, $K D$, effects are be-

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[18] H. O. Pritchard, J. Phys. Chem. **66**, 2111 [1962].

[19] D. J. Seery, J. Phys. Chem. **70**, 1684 [1966].

ing treated on an equal level. Since this coupling is a higher order effect compared to an expansion based on the eigenvectors of the relaxation matrix, ***R***, the selfconsistent theory is analogous to following the evolution of a reacting system over longer periods of time. In other words, the additional information provided by the $\boldsymbol{V P}_n$ expansion is equivalent to the information the kineticist would obtain if he were to follow the reaction over a certain period of time.

Even though it may seem strange, there are precedents for trying to incorporate the accuracy of the measuring process into a physical theory. Most of this work has originated in studies of the uncertainty principle of quantum mechanics. LEVINE has recently emphasized the role of the measuring process in formulating a theory on chemical kinetics [20]. In the next section, we will use a transformation similar to one suggested by Levine to extend the selfconsistent theory to higher order, or over longer periods of time.

IV. Higher Order Terms

A. Self-consistent Theory

The original derivation of the selfconsistent theory and the theory of Ross and Mazur is based on the assumption that the vibrational relaxation time is much smaller than the chemical relaxation time. This is the justification for having the Maxwell-Boltzmann distribution as the leading term in the perturbation expansion. There is no reason for having to make this restrictive assumption. The Maxwell-Boltzmann distribution is our leading term, because we are interested only in the change in concentration of those molecules having an equilibrium distribution. Since we are interested only in the changes occurring over macroscopic intervals of time, we can perform our expansion as follows:

$$[X_2{}^n] = \gamma_n [X_2] + v_1 \gamma_n f_1{}^n + v_2 \gamma_n f_2{}^n + \dots v_m \gamma_n f_m{}^n. \qquad \text{(IV.1a)}$$

The v_n's are related to the rate of change, v, of those molecules having an equilibrium distribution as follows:

$$v = \mathrm{d}[X_2]_{\mathrm{mb}}/\mathrm{d}t = \sum_{m=1} v_m \qquad \text{(IV.1b)}$$

where $[X_2]_{\mathrm{mb}}$ is the number of molecules having an equilibrium distribution. In order to evaluate the $f_m{}^n$, we have o substitute Eq. (III.1) into our original master equation, Eq. (II.2). If we require that v_1 be proportional to the equilibrium velocity, the derivation proceeds in the same manner as our original derivation of Section II. The calculation of the second order contribution involves an expansion of the time derivative, i. e.,

$$\frac{\mathrm{d}[X_2{}^n]}{\mathrm{d}t} = \frac{\mathrm{d}[X_2{}^n]_{\mathrm{mb}}}{\mathrm{d}t} + \frac{\mathrm{d}[X_2{}^n]_{\mathrm{nmb}}}{\mathrm{d}t}. \qquad \text{(IV.1c)}$$

This equation is the velocity analogue of the fact that the molecules in our reacting system can be divided into two groups, those having a Maxwell-Boltzmann distribution (mb) and those that do not (nmb). If Eq. (IV.1a) and Eq. (IV.1b) are used to expand Eq. (IV.1c), it is relatively easy to derive the following formula for the m-th term of the expansion:

$$\left(\frac{\mathrm{d}[X_2{}^n]}{\mathrm{d}t}\right)_m = \gamma_n v_m + \sum_{P=1}^{m-1} \gamma_n f_P{}^n \frac{\mathrm{d}v_P}{\mathrm{d}[X_2]} v_{m-P}\,. \qquad \text{(IV.1d)}$$

The second order correction to the rate of reaction is obtained by solving the following set of simultaneous equations [21,22]:

$$\begin{aligned} &\gamma_n v_2 + \gamma_n f_1{}^n \frac{\mathrm{d}v_1}{\mathrm{d}[X_2]} v_1 \\ &= -k\, d_n \gamma_n \mathrm{f}_2{}^n v_2 + v_2 \Big[\sum_{i \neq n} k_{n,i} f_2{}^i \gamma_i - \sum_{j \neq n} \gamma_n k_{j,n} f_2{}^n \Big]. \end{aligned} \qquad \text{(IV.2a)}$$

The solution to these equations is easily obtained by requiring that

$$v_2 = K(T) \frac{\mathrm{d}v_1}{\mathrm{d}[X_2]} v_1 \qquad \text{(IV.2b)}$$

$$= -K(T) \left[K R_{\mathrm{eq}}[X] + K D_{\mathrm{eq}}\right] v_1\,. \qquad \text{(IV.2c)}$$

We then have

$$\begin{aligned} K(T)\, \gamma_n + \gamma_n f_1{}^n &= -k\, d_{\mathrm{n}} K(T)\, \gamma_n f_2{}^n \\ &\quad + K(T) \Big(\sum_{i \neq n} k_{n\ i} f_2{}^i \gamma_i - \sum_{j \neq n} \gamma_n k_{j,n} f_2{}^n \Big) \end{aligned} \qquad \text{(IV.3)}$$

subject to the constraint $\sum_n \gamma_n f_2{}^n = 0$. Part of our job

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[20] R. D. LEVINE, J. Chem. Phys. **44**, 3597 [1966].

[21] J. O. HIRSCHFELDER, J. Chem. Phys. **26**, 271 [1957].

[22] N. S. SNIDER, J. Chem. Phys. **45**, 3299 [1966]. Contrary to the statement in the introduction of this article, the selfconsistent theory and the theory of Ross and MAZUR can be valid for reacting systems that are not near thermodynamic equilibrium. This problem has been discussed previously in I and by R. B. PARLIN, R. J. MARCUS, and H. EYRING in Proc. Nat. Acad. Sci. U.S. **41**, 900 [1955].

is to evaluate $K(T)$, so these equations have to be solved selfconsistently. This is easily done, because these equations lend themselves to solutions in terms of mean first passage times. The evaluation of the remaining higher order terms proceeds in a similar fashion. While this procedure solves all of the computational aspects of our problem, it offers no physically meaningful clues as to why it works. Beneath the surface of this formalism is a generalization of the conventional steady-state approximation. To see how this comes about, we must carefully reexamine our equations.

B. Steady-State Theory

We were able to learn a great deal about the dissociation of a diatomic molecule by making a change of variables to the Y_n of Eq. (III.3). In a similar manner, the complete master equation for both recombination and dissociation kinetics can be simplified to

$$\mathrm{d}[Y_n]/\mathrm{d}t = k\,r_n \exp(E_n/2\,k\,T)\,[\mathrm{X}]^2 - k\,d_n[Y_n] + \sum_{m\neq 1} k_{n,m}[Y_m]\exp(E_n - E_m)/2\,k\,T - [Y_n]\sum_{m\neq 1} k_{m,n}\,.$$

We have repeatedly emphasized our interest in the change in concentration of those molecules having a Maxwell-Boltzmann distribution. One way of extracting this information from Eq. (IV.4) is to use the projection operator formalism of ZWANZIG and LEVINE[23, 20]. As far as the vector $\mathbf{Y}$ is concerned, the projection operator can be defined by the following equations:

$$P\,\mathbf{Y} = (\mathbf{Y}\cdot\boldsymbol{\gamma}^{1/2})\,\boldsymbol{\gamma}^{1/2} = \Big(\sum_n \mathbf{Y}_n\cdot\gamma_n^{1/2}\Big)\boldsymbol{\gamma}^{1/2} \qquad \text{(IV.4a, b)}$$

where the elements of $\boldsymbol{\gamma}^{1/2}$ are related to the Maxwell-Boltzmann distribution by Eq. (III.9). This formalism is related to the steady-state approximation. Let A be an $N\times N$ matrix whose first row consists of the N elements of the vector $\boldsymbol{\gamma}^{1/2}$, i. e., $A_{1,n} = (\boldsymbol{\gamma}^{1/2})_n$. The other rows are vectors that are orthogonal to $\boldsymbol{\gamma}^{1/2}$, i. e., $\sum_n A_{1,m}\,A_{n,m} = 0$. Multiplying both sides of Eq. (IV.4) by A, we have

$$\frac{\mathrm{d}(A\,Y)_n}{\mathrm{d}t} = K\,R\,\mathrm{X}_n[\mathrm{X}]^2 - \sum_m (A\,K\,D\,A^{-1})_{nm}(A\,Y)_m + \sum_m (A\,R\,A^{-1})_{nm}[A\,Y]_m \qquad \text{(IV.5a)}$$

where

$$K\,R\,\mathrm{X}_n = \sum_m A_{nm}\,k\,r_m \exp(E_m/2\,k\,T)\,, \qquad \text{(IV.5b)}$$

$$K\,D_{nm} = k\,d_n\,\delta_{n,m}\,, \qquad \text{(IV.5c)}$$

$$R_{n,m} = k_{n,m}\exp(E_n - E_m)/2\,k\,T\,, \qquad \text{(IV.5d)}$$

$$R_{n,n} = -\sum_{m\neq n} k_{m,n}\,. \qquad \text{(IV.5e)}$$

Even though Eq. (IV.5) is equivalent to our original master equation, it is better suited for relating our work to the conventional steady-state approximation. The selfconsistent theory and the method of Ross and Mazur are equivalent to the steady-state approximation in "$A\,Y$ space". Since

$$A_{1,n} = (\boldsymbol{\gamma}^{1/2})_n \quad \text{and} \quad \mathbf{Y}_n = [\mathrm{X}_2{}^n]\ \mathrm{X}\exp(E_n/2\,k\,T)\,,$$

$(A\,Y)_1 = [\mathrm{X}_2(t)]/(\sum_n \exp(-E_n/k\,T))^{1/2}$ is proportional to the total number of molecules, $[\mathrm{X}_2] = \sum_n [\mathrm{X}_2{}^n]$. This result has a number of interesting implications. The kineticist follows the evolution of a recombination or dissociation reaction by measuring the change in the total number of molecules. Our theorem says that he is also measuring the change in concentration of those molecules having a Maxwell-Boltzmann distribution. If we were to divide the $[\mathrm{X}_2{}^n(t)]$ into N groups, the time dependence of the group corresponding to the Maxwell-Boltzmann distribution, $\boldsymbol{\gamma}^{1/2}$, would be the same as the change in the total number of molecules, $[\mathrm{X}_2(t)]$. It is always tempting to speculate about the physical significance of a mathematical formalism. As far as recombination reactions are concerned, the physical implications of our formalism are something we already know; all the highly excited molecules formed in a recombination reaction will eventually relax to a Boltzmann distribution. As far as dissociation reactions are concerned, the physical implications are less obvious. For every Z molecule dissociated, the system loses its ability to have Z molecules with a Maxwell-Boltzmann distribution. While this interpretation may not be very appealing, we should recall that we are interested ony in deriving a macroscopic theory. On the macroscopic time scale, the reaction is usually slow enough to justify our equating the rate of dissociation to the rate of disappearance of molecules with a Boltzmann distribution.

Up to now, our discussion has been mathematically rigorous. In order to derive a macroscopic theory of chemical kinetics, it is again necessary to make the classical distinction between the microscopic and macroscopic evolution of a reacting system. The kineticist follows the progress of a reaction by continuously measuring the concentration of the

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[23] R. ZWANZIG, J. Chem. Phys. **33**, 1338 [1960].

reactants or products. As we have indicated in the previous paragraph, all of tthis experimental information is contained in the equation for $\mathrm{d}(A\,Y)_1/\mathrm{d}t$ of Eq. (IV.5a). In other words, this equation describes the slow macroscopic evolution of a reacting system, and the remaining equations describe the fast microscopic evolution. The actual distinction between the time scales characterizing the microscopic and macroscopic behavior is governed by our choice of A. If the rate of relaxation is much faster than the rate of reaction, i. e., the rate constants associated with vibrational transitions are larger than those for dissociation, the relaxation of the internal energy levels is *almost* independent of the reaction. Under these conditions, the eigenvectors of the relaxation matrix R appearing in Eq. (IV.5d) are a "natural" basis for constructing A. This choice obviously guarantees $(A\,R\,A^{-1})$ being diagonal. This derivation now proceeds in the spirit of the steady-state approximation. On the macroscopic time scale, the rate of reaction is

$$v = \sum_{n=0} v_n = N \cdot \mathrm{d}(A\,Y)_1/\mathrm{d}t \qquad \text{(IV.6a)}$$

where $$N = \sum_m \exp(-E_n/k\,T)\,]^{1/2}.$$

Since the lowest eigenvalue of R vanishes

$$v_0 = N[K\,R\,\mathrm{X}_0[\mathrm{X}]^2 - \sum_m (A\,K\,D\,A^{-1})_{nm} (A\,Y)_m]\,. \qquad \text{(IV.6b)}$$

If the leading term in the analogous expansions of $(A\,Y)$ is $N(A\,Y)_1{}^0 = [\mathrm{X}_2]$ and $(A\,Y)_m{}^0 = 0$, Eq. (IV.6b) is proportional to the equilibrium rate of reaction.

The higher order contributions to the reaction rate depend on the other terms in the expansion of $(A\,Y)$. These terms contain information about the fast microscopic motion of our reacting system, or how the internal energy levels relax to a Maxwell-Boltzmann distribution. Since the relaxation occurs almost instantaneously compared to the rate of reaction, $\mathrm{d}(A\,Y)_n{}^0/\mathrm{d}t = 0$, to first approximation. Since only the macroscopic behavior of our system is of interest, we can express the time dependence of the $(A\,Y)^1$ in terms of the reaction rate, i. e., $(A\,Y)_m{}^1 = L_m\,v_0$. Substituting this expression into our quasiequilibrium equation, we obtain the following set of equations:

$$K\,R\,\mathrm{X}_n[\mathrm{X}]^2 - (A\,K\,D\,A^{-1})_{n1}(A\,Y)_1{}^0 + v_0\,\lambda_n\,L_n = 0\,, \qquad \text{(IV.7a)}$$

$$\sum_m \exp(E_m/2\,k\,T)\;A_{nm}\{[\mathrm{X}]^2\,k\,r_m - \gamma_m\,k\,d_m[\mathrm{X}_2]\} + v_0\,\lambda_n\,L_n = 0\,, \qquad \text{(IV.7b)}$$

$$-\sum_m A_{nm}\,k\,d_m\,\gamma_m{}^{1/2}/\lambda_n = N\,L_n\,. \qquad \text{(IV.7c)}$$

In going from Eq. (IV.7b) o (IV.7c), we made use of Eq. (II.8).

As we have already indicated in the discussion following Eq. (III.15), Eq. (IV.7) is equivalent to the equations arising in the work of Ross et al. If we were to solve Eq. (III.12) by expanding $\boldsymbol{U}^1$ in terms of the eigenvectors of the relaxation matrix, R, i. e.,

$$\boldsymbol{U}^1 = \sum_n C_n\,\boldsymbol{V}_n \qquad \text{(IV.8)}$$

we would find that the C_n are equal to the L_n. Since Eq. (III.12) is one of the equations arising in the theory of Pyun and Ross, Eq. (IV.7c) must also be equivalent to their equation. The higher order equations can be derived by a straight-forward application of the steady-state approximation in "$A\,Y$ space". However, the number of equations to be solved increases at each stage of the calculation. In order to obtain the second order contribution, two sets of equations must be solved. Since this problem does not arise with the selfconsistent theory, it is more profitable to turn our attention to the relationship between this theory and the steady-state approximation.

The derivation of the steady-state analogue of the selfconsistent theory also starts with Eq. (IV.5a). It differs from the previous derivation in the exact form of the matrix, A. In order to keep track of those molecules having a Maxwell-Boltzmann distribution, the elements of the first row are still, $A_{1n} = \Upsilon_n{}^{1/2}$. Each of the other rows consists of the $N-1$ eigenvectors $\boldsymbol{V}\boldsymbol{P}_n$ of Eq. (III.34). The first term in our new expansion of $(A\,Y)$ is still the Maxwell-Boltzmann distribution, i. e., $N(A\,Y)_1{}^0 = [\mathrm{X}_2]$ and $(A\,Y)_m{}^0 = 0$; thus, the first term in our expression for the rate of reaction is the equilibrium velocity v_0. In order to evaluate the higher order terms in our expansion, it is again necessary to make a distinction between the macroscopic and microscopic evolution of the reacting system. We are not, however, going to make any assumptions about the rate of relaxation being much faster than the rate of reaction. In certain systems, the characteristic times for reaction and vibrational relaxation are almost equal, because the rate of relaxation is the rate controlling step in determining the rate of reaction[18, 19]. As we shall see, his effect is incorporated into the selfconsistent theory via the vectors $\boldsymbol{V}\boldsymbol{P}_n$. These vectors are really the eigenvectors of the matrix $Q(R-KD)\,Q$, where $Q=I-P$, I is the unit matrix, and the projection operator P is defined as follows[24, 25]:

$$P\,\boldsymbol{V} = (\boldsymbol{\gamma}^{1/2}\cdot\boldsymbol{V})\,\boldsymbol{\gamma}^{1/2}. \qquad \text{(IV.9)}$$

On the macroscopic time scale, we are interested only in the change in the number of molecules having a Maxwell-Boltzmann distribution. Since this information has been projected out of the $\boldsymbol{V}\boldsymbol{P}_n$, these vectors must be associated with the fast microscopic motion. To a first approximation, $\mathrm{d}(A\,Y)_n^{\,0}/\mathrm{d}t=0$ for $n \neq 1$. If we express the time dependence of the $(A\,Y)^1$ in terms of the velocity of reaction, i. e., $(A\,Y)_m^{\,1}=K_m\,v_0$, we can derive a set of equations analogous to Eq. (IV.7):

$$K\,R\,\mathrm{X}_n[\mathrm{X}]^2-(A\,K\,D\,A^{-1})_{n1}(A\,Y)_1^{\,0} \qquad \text{(IV.10a)}$$
$$+\sum_{m\neq 1}[A(R-K\,D)\;A^{-1}]_{nm}\;(A\,Y)_m^{\,1}=0\,,\;n\neq 1$$

$$\sum_P \exp(E_P/2\,k\,T)\;A_{nP}\,\{[\mathrm{X}]^2\,k\,r_{\mathrm{P}}-\gamma_P\,k\,d_P[\mathrm{X}_2]\}$$
$$+v_0\,\lambda\,P_n\,K_n=0\,, \qquad \text{(IV.10b)}$$

$$-\sum_n A_{mn}\,k\,d_n\,\gamma_n^{1/2}/(N\,\lambda\,P_n)=K_m\,. \qquad \text{(IV.10c)}$$

In oorder to obtain the first order correction to the rate of reaction, we need an equation describing the change in the number of molecules having a Boltzmann distribution, i. e.,

$$v=N\Big[K\,R\,\mathrm{X}_1[\mathrm{X}]^2-\sum_m (A\,K\,D\,A^{-1})_{1m}(A\,Y)_m\Big]. \qquad \text{(IV.11a)}$$

As far as our interests are concerned, this equation can be simplified to

$$v=\sum_n k\,r_n[\mathrm{X}]^2-\sum_n \gamma_n\,k\,d_n[\mathrm{X}_2] \qquad \text{(IV.11b)}$$
$$+N\sum_{m\neq 1}[A(R-K\,D)\;A^{-1}]_{1m}\;(A\,Y)_m^{\,1}$$

$$=v_0+N\,v_0\sum_{m\neq 1}[A(R-K\,D)\;A^{-1}{}_{1m}\,K_m \qquad \text{(IV.11c)}$$

$$=v_0-v_0\sum_{m,P}(A_{mP}\,k\,d_P\,\gamma_P^{1/2})^2/\lambda_m\,. \qquad \text{(IV.11d)}$$

While it is not obvious, Eq. (IV.11) is equivalent to the selfconsistent expression for the rate of reaction. As we have already indicated, Eq. (III.23) is equivalent to Eq. (II.7). Since it is relatively easy to show that Eq. (IV.11) and Eq. (III.23) are identical, the equivalence of Eq. (II.7) and Eq. (IV.11) follows immediately. It is also relatively easy to derive the higher order selfconsistent equations from this formalism. Once the $(A\,Y)_m^{\,n}$ have been calculated, the corresponding term in the expansion of $\mathrm{d}(A\,Y)_m/\mathrm{d}t$ can be obtained, i. e.,

$$\frac{\mathrm{d}(A\,Y)_m}{\mathrm{d}t}=\frac{\mathrm{d}(A\,Y)_m^{\,0}}{\mathrm{d}t}+\frac{\mathrm{d}(A\,Y)_m^{\,1}}{\mathrm{d}t}+\dots \qquad \text{(IV.12a)}$$

$$=O+K_m\frac{\mathrm{d}v_0}{\mathrm{d}t}+\dots \qquad \text{(IV.12b)}$$

for $m\neq 1$. Substituting the second term of Eq. (IV.12) and the third term of the expansion,

$$(A\,Y)_m=(A\,Y)_m^{\,0}+(A\,Y)_m^{\,1}+(A\,Y)_m^{\,2}+\dots\,, \qquad \text{(IV.13a)}$$

into Eq. (IV.5), yields a set of equations of the form

$$\sum_{m\neq 1}[A(R-K\,D)\;A^{-1}]_{nm}\;(A\,Y)_m^{\,2}=K_m\,\mathrm{d}v_0/\,\mathrm{d}t\,. \qquad \text{(IV.13b)}$$

These equations are easily solved by expressing the time dependence of the $(A\,Y)_m^{\,2}$ in terms of the macroscopic variable,

$$\mathrm{d}(A\,Y)_m^{\,1}/\mathrm{d}t,\quad \text{i. e.,}\quad (A\,Y)_m^{\,2}=L_m(\mathrm{d}v_0/\mathrm{d}t)\,.$$

Once the $(A\,Y)_m^{\,2}$ are evaluated, the next term in the expansion can be obtained from Eq. (IV.11).

Even though this steady-state formalism provides a number of insights about the selfconsistent theory, the need to have a knowledge of a large number of eigenvectors and eigenvalues makes it almost useless a far as numerical calculations are concerned. The original formulation of the selfconsistent theory is better suited for this purpose. The equations arising in the theory of Pyun and Ross, and the selfconsistent theory can also be solved by variational methods, analogous to the variational method for solving the Boltzmann equation[26]. Solving the equations of Pyun and Ross is equivalent to finding the extreme value of the functional

$$J(\boldsymbol{U})=-(\boldsymbol{U}\cdot R\,\boldsymbol{U})+2(\boldsymbol{U}\cdot K\,D\,\boldsymbol{\gamma}^{1/2}) \qquad \text{(IV.14)}$$

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[24] G. Speisman, Phys. Rev. **107**, 1180 [1957].

[25] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 [1962].

[26] J. T. O'Toole and J. S. Dahler, J. Chem. Phys. **35**, 19 [1961].

subject to the constraint $\boldsymbol{U} \cdot \boldsymbol{\gamma}^{1/2} = 0$. The variational expression for the selfconsistent theory is obtained by replacing the R in the first term of Eq. (IV.14) by $R - K\,D$[27].

V. Conclusions

Over the past decade, a number of different mathematical and physical insights about the importance of nonequilibrium effects in chemical kinetics have led to the formulation of several theories of recombination-dissociation kinetics. While each of these theories has contributed to our understanding of this problem, the number of different approaches to this problem gives rise to questions about the validity of each of these theories. One of the important implications of this work is that many of these theories are equivalent. Our analysis of the selfconsistent theory contains a number of references to other theories. Not only does the concept of a mean first passage time play an important role in solving the selfconsistent equations, but the leading term in our expansion for the dissociation rate constant is equal to the inverse of the mean first passage time for a Maxwell-Boltzmann distribution. If the higher order terms arising in the selfconsistent theory and the theory of Pyun and Ross were to be evaluated, the dislocation rate constant for each of these theories would be identical and equal to the eigenvalue that plays an important role in theories of unimolecular decomposition[28]. The leading term in an expansion of this eigenvalue is the mean first passage time for a Boltzmann distribution. All of these methods can also be derived from a generalization of the conventional steady-state approximation. The equivalence of all these theories originates from an attempt to describe the slow macroscopic motion of a very complicated process in terms of the average behavior of its fast microscopic motion. The ultimate test of the validity of these theories will be their ability to predict rate constants. Once the transition probabilities needd for the evaluation of these rate constants for some simple reaction like,

$$H + H_2 \rightarrow H + H + H,$$

are available, it will be possible to make a more meaningful evaluation of these theories.

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[27] B. Widom, Advan. Chem. Phys. **5**, 353 [1963].

[28] W. G. Valance and E. W. Schlag, J. Chem. Phys. **45**, 4280 [1966].