Diffusion Theory of Nonequilibrium Dissociation and Recombination*

JAMES KECK

Avco-Everett Research Laboratory, Everett, Massachusetts

AND

GEORGE CARRIER

Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts

(Received 15 March 1965)

The coupled vibration–dissociation–recombination process for molecules and atoms has been examined. Techniques for solving the appropriate master equations for both quantum (discrete) and classical (continuous) models are given. It is shown that the process is most easily treated classically and that in this case the master equation can be reduced to an equivalent diffusion equation. It is assumed that, after an initial vibration transient, during which reactions are negligible, the process may be treated using the steady-state approximation. During the steady-state phase, the usual phenomenological rate equations are valid and the ratio of the forward and reverse rate constants is the equilibrium constant, though the individual rate constants are depressed below their equilibrium values.

Comparison of the results with other theoretical work shows general agreement for similar models; comparison with shock-tube experiments on molecular dissociation and stellarator experiments on ionic recombination is encouraging.

I. INTRODUCTION

THE time-dependent relaxation of a dilute mixture of molecules dissociating (or recombining) in a background of inert atoms is a fundamental process in chemical kinetics and has been the subject of numerous experimental and theoretical investigations. Excellent surveys of past work on this problem may be found in review articles by Osipov and Stupochenko,[1] Widom,[2] and Rice.[3] The basic master equations governing the relaxation process have been formulated, and the general properties of their solutions have been studied.[1,2] However, detailed solutions of these equations for models which provide a physically reasonable description of an atom interacting with a molecule have not yet been obtained. Although most of the current theories[4–18] predict the order of magnitude of

the observed steady-state rate constants and the incubation time observed in dissociation experiments[19] has been qualitatively explained,[20] a satisfactory understanding of the dependence of the rate constants on temperature and atomic species is still lacking. In addition, the question of whether the ratio of the observed dissociation and recombination rate constants is equal to the equilibrium constant is still being debated.[14,21–28]

The difficulties are due in part to the different assumptions made in treating the mechanics of the process and in part to the lack of knowledge of the interaction potential involved. In this connection, it should be observed that an acceptable solution of the mechanical problem must be obtained before serious consideration can be given to the effects of the potential. Given such a solution, it should then be possible to use the experimental data to obtain information about the interaction potential and this, we believe, is an important goal of current research on the theory of elementary chemical reactions.

In the present paper, we have attempted to take a step toward this goal by investigating the solutions of the appropriate master equations for physically reasonable atomic models. In so doing, we have reviewed the solutions for some of the simpler models treated previously and tried to indicate their deficiencies. The molecular models considered include both Morse and Coulomb oscillators. Solutions of the appropriate

[1] A. I. Osipov and E. V. Stupochenko, Soviet Phys.—Usp. **6**, 47 (1963) [Usp. Fiz. Nauk. **79**, 81 (1963)].
[2] B. Widom, Advan. Chem. Phys. **5**, 353 (1963).
[3] O. K. Rice, 50th Anniversary Solvay Conference, Brussels, Belgium, November 1962.
[4] C. F. Hansen, AIAA J. **3**, 61 (1965).
[5] S. E. Nielson and T. A. Bak, J. Chem. Phys. **41**, 665 (1964).
[6] T. A. Bak and J. L. Lebowitz, Phys. Rev. **131**, 1138 (1963).
[7] S. W. Benson and T. Fueno, J. Chem. Phys. **36**, 1597 (1962).
[8] J. C. Light, J. Chem. Phys. **36**, 1016 (1962).
[9] F. T. Smith, Discussions Faraday Soc. **33**, 183 (1962).
[10] O. K. Rice, J. Phys. Chem. **67**, 6 (1962).
[11] H. O. Pritchard, J. Phys. Chem. **65**, 504 (1961).
[12] E. Bauer and M. Salkoff, J. Chem. Phys. **33**, 1202 (1962).
[13] J. C. Keck, J. Chem. Phys. **32**, 1035 (1960); **29**, 410 (1958).
[14] E. E. Nikitin and N. D. Sokolov, J. Chem. Phys. **31**, 1371 (1959).
[15] D. L. Bunker and N. Davidson, J. Am. Chem. Soc. **80**, 5085 (1958).
[16] E. W. Montroll and K. E. Shuler, Advan. Chem. Phys. **1**, 361 (1958).
[17] E. V. Stupochenko and A. I. Osipov, Zh. Fiz. Khim. **33**, 1526 (1959).
[18] E. Wigner, J. Chem. Phys. **5**, 720 (1937).

[19] K. L. Wray, J. Chem. Phys. **37**, 1254 (1962).
[20] P. V. Marrone and C. E. Treanor, Phys. Fluids **6**, 1215 (1963).
[21] N. S. Snider, J. Chem. Phys. **42**, 548 (1965).
[22] N. S. Snider, Princeton University thesis, TR 5, January 1964, NASA 64-15957.
[23] C. W. Pyun and J. Ross, J. Chem. Phys. **40**, 2572 (1964).
[24] O. K. Rice, J. Phys. Chem. **67**, 1733 (1963); **65**, 1972 (1961).
[25] H. O. Pritchard, J. Phys. Chem. **66**, 2111 (1962).
[26] E. E. Nikitin, Kinetika i Kataliz **3**, 830 (1962).
[27] B. Widom, J. Chem. Phys. **34**, 2050 (1961).
[28] J. C. Polanyi, J. Chem. Phys. **31**, 1338 (1959).

master equations have been investigated for both classical (continuous) and quantum- (discrete) mechanical cases. It is assumed that for either dissociation or recombination the relaxation process starts with an initial fast transient having a duration of the order of the vibrational relaxation time during which there is negligible chemical reaction but the population of the vibrational levels approaches a distribution which is extremely close to a solution of the steady-state master equations. This transient is followed by a very much slower phase during which the steady-state distribution is maintained and the chemical reaction proceeds to equilibrium. For dissociation, the steady-state distribution is very nearly Boltzmann except near the dissociation limit where the levels are underpopulated; for recombination, the steady-state distribution is Boltzmann near the dissociation limit but the lower levels are underpopulated. During the steady-state phase of the relaxation process, the evolution of the system is described by the usual phenomenological equation,

$$dM(t)/dt = k_r A^2(t) - k_d M(t), \qquad (1.1)$$

where $M(t)$ is the molecule concentration, $A(t)$ is the atom concentration, and the ratio of the steady-state dissociation and recombination rate constants, k_d/k_r, is equal to the equilibrium constant, A_e^2/M_e. This result is in complete accord with the conclusions of Stupochenko and Osipov,[17] Snider,[20] Nikitin,[24] and Rice[22] and justifies the experimental practice of using the equilibrium constant to relate the dissociation and recombination rate constants.

It is also shown that because of the high level density near the dissociation limit the classical master equation is appropriate for treating dissociation and recombination and that in the limit of small energy transfers this integrodifferential equation may be reduced to an equivalent diffusion equation. The diffusion equation is simpler than the original master equation and provides considerable physical insight into the relaxation process by making possible a direct comparison with familiar heat-flow problems. The available information on the average energy transfer in collisions[29,30] indicates that it should be a reasonable approximation in practice. This approach is similar to one originally proposed by Kramers[31-33] in which the relaxation of a chemical system was described in terms of a viscous diffusion process governed by a Fokker–Planck equation.

A comparison of the theoretical rate constants with the shock-tube data on the dissociation of hydrogen,[34-37]

nitrogen,[38,39] oxygen,[40-45] fluorine,[46] chlorine,[47,48] bromine,[49-53] and iodine[54] by inert gases shows reasonable agreement considering the uncertainties in experimental data and the three-body potentials, and relatively small changes in the assumed ranges of the interactions will produce almost complete agreement. It is premature to take such changes too seriously, however.

The theory may also be applied to the ionization and recombination of atoms and a calculation of the population distribution for a recombining He$^+$ plasma has been made, which is in good agreement with the experimental results of Hinnov and Hirschberg.[55]

In the following section, we set down the master equations on which our models of the relaxation process are based and consider the general consequences of the steady-state assumption as applied to these equations. In Sec. III we show two methods by which the classical master equation may be reduced to an equivalent diffusion equation. In Sec. IV, we derive the steady-state solutions of the master equations for both quantum and classical molecular models and compare the results with the experimental data. In Sec. V, we briefly summarize our conclusions.

II. MASTER EQUATIONS AND SOME GENERAL IMPLICATIONS

We confine our attention to gas mixtures which consist primarily of inert gas atoms diluted slightly by diatomic molecules. We consider situations in which, at time zero, the background gas is given a new translational temperature. We ignore the very small time interval during which the translational and rotational equilibria are established, but study in detail the manner in which the vibrational relaxation, dissociation, and recombination processes contribute to the evolution of the state of the molecular gas.

The dilute character of the gas mentioned above implies that molecule–molecule collisions will be of no

[29] B. Woznick, J. Chem. Phys. **42**, 1151 (1965) (also private communication).

[30] J. C. Keck, Discussions Faraday Soc. **33**, 173 (1962).

[31] H. A. Kramers, Physica **7**, 284 (1940).

[32] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

[33] H. C. Brinkman, Physica **22**, 29, 149 (1956).

[34] E. A. Sutton, J. Chem. Phys. **36**, 2923 (1962).

[35] R. W. Patch, J. Chem. Phys. **36**, 1919 (1962).

[36] J. P. Rink, J. Chem. Phys. **36**, 1398, 262 (1962).

[37] W. C. Gardiner, Jr., and G. B. Kistiakowsky, J. Chem. Phys. **35**, 1765 (1961).

[38] B. Cary, Phys. Fluids **8**, 26 (1965).

[39] S. Byron, *Proceedings of the Ninth General Assembly of AGARD* (NATO Aachen, 1959).

[40] K. L. Wray, J. Chem. Phys. **38**, 1518 (1963); **37**, 1254 (1962).

[41] J. P. Rink, J. Chem. Phys. **36**, 572 (1962).

[42] J. Rink, H. Knight, and R. Duff, J. Chem. Phys. **34**, 1942 (1961).

[43] M. Camac and A. Vaughan, J. Chem. Phys. **34**, 460 (1961).

[44] S. R. Byron, J. Chem. Phys. **30**, 1380 (1959).

[45] J. P. Chesnick and G. B. Kistiakowsky, J. Chem. Phys. **38**, 956 (1958).

[46] C. D. Johnson and D. Britton, J. Phys. Chem. **68**, 3032 (1964).

[47] T. A. Jacobs and R. R. Giedt, J. Chem. Phys. **39**, 749 (1963).

[48] H. Hiraoka and R. Hardwick, J. Chem. Phys. **36**, 1715 (1962).

[49] C. D. Johnson and D. Britton, J. Chem. Phys. **38**, 1455 (1963).

[50] G. Burns and D. F. Hornig, Can. J. Chem. **38**, 1702 (1960).

[51] D. Britton, J. Phys. Chem. **64**, 742 (1960).

[52] H. B. Palmer and D. F. Hornig, J. Chem. Phys. **26**, 98 (1957).

[53] D. Britton and N. Davidson, J. Chem. Phys. **25**, 810 (1956).

[54] D. Britton, N. Davidson, W. Gehman, and G. Schott, J. Chem. Phys. **25**, 804 (1956).

[55] E. I. Hinnov and J. G. Hirschberg, Phys. Rev. **125**, 795 (1962).

importance compared to the molecule–atom collisions in either the vibrational relaxation processes or the dissociation process. Furthermore, in the recombination process, only collisions among a background atom and the two recombining particles will contribute effectively to the phenomenon.

The mathematical models which can be used to describe this evolution depend on a detailed characterization of the molecules making up the gas under study. However, each such model involves a probabilistically inferred rate at which molecules leave any given state and enter any other state. The quantum-mechanical version of any such model, then, is of the form

$$\frac{\partial N(n, t)}{\partial t} = \sum_{m=0}^{P-1} [B(n, m)N(m, t) - B(m, n)N(n, t)]$$
$$+ B(n, c)A^2(t) - B(c, n)N(n, t), \quad (2.1)$$

where $N(n, t)$ is the concentration of molecules in the nth vibrational level, P is the number of levels in the molecule, and $A(t)$ is the concentration of atoms resulting from dissociation. This equation merely states that molecules may leave the level n by making transitions to the level m at a rate $B(m, n) \ N(n, t)$, or dissociating to the continuum at a rate $B(c, n) \ N(n, t)$ and may enter the level n by making transitions from the level m at a rate $B(n, m) \ N(m, t)$, or recombining from the continuum at a rate $B(n, c) \ A^2$. The form of the equation is a consequence of our assumptions that (1) the majority of the transitions are induced by collisions with a background atom, (2) the state of the molecules can be described by the vibrational quantum number, and (3) recombination requires a three-body collision.

Although our model contains no explicit reference to the rotational quantum number and it may therefore appear that rotational effects are to be omitted, this is not the case. Within the framework of this model rotational effects may be approximately taken into account by using an appropriate effective potential to describe the molecule and by measuring the vibrational energy from the top of the rotational barrier. In Sec. IV this technique is used in treating the classical Morse oscillator.

At thermodynamic equilibrium, $\partial N(n, t)/\partial t$ is zero, and the requirement of detailed balancing leads to the conditions

$$R(m, n) = B(m, n)N_e(n) = B(n, m)N_e(m) = R(n, m),$$
$$(2.2a)$$

$$R(c, n) = B(c, n)N_e(n) = B(n, c)A_e^2 = R(n, c), \quad (2.2b)$$

where $N_e(n) = N_e(0)e^{-\epsilon_n}$ is the equilibrium concentration of molecules in the level n, $\epsilon_n = E_n/kT$ is the energy of the level in units of kT, A_e is the equilibrium atom concentration, $R(n, m)$ is the "one-way" equilib-

rium transition rate between the levels n and m and $R(c, n)$ is the "one-way" equilibrium dissociation rate. In writing (2.2), we have used our assumption that the translational and rotational degrees of freedom of the molecule are in equilibrium with the translational degree of freedom of the background atoms so that the transition probabilities are the same under the nonequilibrium conditions of interest as they are at full equilibrium.

Using (2.2), and introducing the specific population

$$X(n, t) = N(n, t)/N_e(n), \quad (2.3)$$

which is the ratio of the actual concentration of molecules in the level n to the equilibrium concentration, (2.1) can be written in the more symmetrical form

$$N_e(n)\frac{\partial X(n, t)}{\partial t} = \sum_{m=0}^{P-1} R(n, m)[X(m, t) - X(n, t)]$$
$$+ R(c, n)\{[A(t)/A_e]^2 - X(n, t)\}. \quad (2.4)$$

As is seen later, the use of $X(n, t)$ is convenient not only because it reduces (2.1) to a simpler equation, but also because it varies less with n than $N(n, t)$ and enables one to see more clearly the manner in which the nonequilibrium solutions of (2.1) depart from a Boltzmann distribution.

The classical analog of (2.4) has the form

$$N_e(\epsilon)\frac{\partial X(\epsilon, t)}{\partial t} = \int_0^\delta R(\epsilon, \epsilon')[X(\epsilon', t) - X(\epsilon, t)]d\epsilon'$$
$$+ R(c, \epsilon)\{[A(t)/A_e]^2 - X(\epsilon, t)\}, \quad (2.5)$$

where $N_e(\epsilon) = N_e(0)\rho(\epsilon)e^{-\epsilon}$ is the equilibrium concentration of molecules per unit energy range at ϵ, $\rho(\epsilon)$ is the ratio of the level density at ϵ to that at 0,

$$X(\epsilon, t) = N(\epsilon, t)/N_e(\epsilon) \quad (2.6)$$

is the ratio of the concentration of molecules, $N(\epsilon, t)$, to the equilibrium concentration, $R(\epsilon, \epsilon')d\epsilon'd\epsilon$ is the "one-way" equilibrium rate of transitions from an energy band $d\epsilon$ at ϵ to an energy band $d\epsilon'$ at ϵ', $R(c, \epsilon)d\epsilon$ is the "one-way" equilibrium dissociation rate from an energy band $d\epsilon$ at ϵ, and $\delta = D/kT$ is the dissociation energy in units of kT.

General Steady-State Implications

Before proceeding with the detailed solution and application of the master equations (2.4) and (2.5) we should like to summarize a few important results which may be obtained using the conventional steady-state approximation. In so doing, we consider a gas mixture of the type previously discussed, whose temperature is suddenly changed so that the molecules are thrown out of equilibrium. As may be inferred

from the work of Montroll and Schuler,[16] the sequence of events for all situations except those involving very high temperatures begins with a rapid relaxation to a population distribution which is *almost* a Boltzmann distribution. This initial phase, during which dissociation and recombination are negligible, is followed by a much slower phase during which most of the dissociation or recombination occurs and the "almost Boltzmann" distribution is maintained. During this phase of the process we anticipate that our "almost Boltzmann" distribution will be closely approximated by a solution of the equation

$$\sum_{m=1}^{P-1} R(n, m)[X(m, t) - X(n, t)]$$
$$+ R(c, n)\{[A(t)/A_e]^2 - X(n, t)\} = 0, \quad (2.7)$$

and we seek solutions of (2.7) of the form

$$[A(t)/A_e]^2 - X(n, t) = f(t)\chi(n). \quad (2.8)$$

Substituting (2.8) into (2.7) shows that $\chi(n)$ satisfies the equation

$$\sum_{m=0}^{P-1} R(n, m)[\chi(m) - \chi(n)] - R(c, n)\chi(n) = 0, \quad (2.9)$$

which determines the steady-state distribution when recombination is negligible.

Imposing the normalization $\chi(0) = 1$ in (2.8) we obtain

$$X(n, t) = X(0, t)\chi(n) + [A(t)/A_e]^2[1 - \chi(n)], \quad (2.10)$$

and the time-dependent functions may now be determined by summing (2.4) over n and substituting (2.10) into the result. This gives

$$\frac{dM(t)}{dt} = \left\{\left[\frac{A(t)}{A_e}\right]^2 - X(0, t)\right\} \sum_{n=0}^{P-1} R(c, n)\chi(n), \quad (2.11)$$

where

$$M(t) = \sum_{n=0}^{P-1} N_e(n)X(n, t) \quad (2.12)$$

is the concentration of molecules,

$$M(t) = \sum_{n=0}^{P-1} N_e(n)\{X(0, t)\chi(n)$$
$$+ [A(t)/A_e]^2[1 - \chi(n)]\}. \quad (2.13)$$

It now follows from our assumption of an "almost Boltzmann" distribution, that $\chi(n) \approx 1$ everywhere except near the dissociation limit. Thus whenever $X(0, t)$ is appreciable compared to $[A(t)/A_e]^2$

$$M(t) \approx X(0, t) \sum_{n=0}^{P-1} N_e(n) = X(0, t)M_e, \quad (2.14)$$

so that (2.11) can be written in the form

$$dM(t)/dt \approx k_r A^2(t) - k_d M(t), \quad (2.15)$$

where

$$k_r = \sum_{n=1}^{P-1} R(c, n)\chi(n)/A_e^2 \quad (2.16)$$

and

$$k_d = \sum_{n=1}^{P-1} R(c, n)\chi(n)/M_e, \quad (2.17)$$

are, by definition, the steady-state recombination and dissociation rate constants.

Equation (2.15) is identical to the standard rate equation used for describing the dissociation recombination process. It can be solved in conjunction with the conservation equation

$$2M(t) + A(t) = A_0 \quad (2.18)$$

to give a complete history of the dissociation–recombination process for the steady-state phase following the vibrational transient. Note that the use of (2.15) is not restricted by our assumption that $X(0, t) \sim [A(t)/A_e]^2$ since for $X(0, t) \ll [A(t)/A_e]^2$ the dissociation terms in both (2.11) and (2.15) may be neglected.

The equilibrium rate constants corresponding to (2.16) and (2.17) are

$$k_{re} = \sum_{n=0}^{P-1} R(c, n)/A_e^2 \quad (2.19)$$

and

$$k_{de} = \sum_{n=0}^{P-1} R(c, n)/M_e, \quad (2.20)$$

and it follows that

$$k_d/k_r = k_{de}/k_{re} = A_e^2/M_e, \quad (2.21)$$

where A_e^2/M_e is the equilibrium constant for the reaction.

These results are in accord with arguments advanced by Stupochenko and Osipov,[17] Rice,[24] and Snider,[22] but disagree with the early conclusions of Nikitin and Sokolov.[14] The reason is that, as Rice has pointed out, Nikitin and Sokolov failed to take account of the redissociation of the molecules near the dissociation limit. Thus, while it is true that atoms recombine at a rate which is the same in the nonequilibrium and equilibrium situations as long as the translational distribution of the atoms is at equilibrium, it is not true that this represents the *net* rate of appearance of molecules which is the quantity measured experimentally during the steady-state phase.

The same procedure may be followed to obtain a steady-state solution for the classical model of (2.5).

In this case the specific distribution is

$$X(\epsilon, t) = X(0, t)\chi(\epsilon) + [A(t)/A_e]^2[1-\chi(\epsilon)], \quad (2.22)$$

where $\chi(\epsilon)$ satisfies the equation

$$\int_0^\delta R(\epsilon, \epsilon')[\chi(\epsilon') - \chi(\epsilon)]d\epsilon' - R(c, \epsilon)\chi(\epsilon) = 0, \quad (2.23)$$

and the steady-state rate constants analogous to (2.16) and (2.17) are

$$k_r = \int_0^\delta \frac{R(c, \epsilon)\chi(\epsilon)d\epsilon}{A_e^2}, \quad (2.24)$$

and

$$k_d = \int_0^\delta \frac{R(c, \epsilon)\chi(\epsilon)d\epsilon}{M_e}. \quad (2.25)$$

In concluding this discussion it should be pointed out that Eq. (2.15) is a consequence of the form of (2.8) assumed for the steady-state distribution function and the uniqueness of the solution has not been proved. Further examination of this point is required.

III. EQUIVALENT DIFFUSION EQUATIONS

An alternative method of describing the vibrational relaxation process in the classical limit involves the transformation of the master equation (2.5) to an equivalent diffusion equation. The procedure is analogous to that by which the master equation may be reduced to the Fokker–Planck equation.[6,56] It leads to the identification of a chemical reaction with a diffusion process in phase space as proposed by Kramers[31-33] and connects the diffusion coefficient with the moments of the transition kernel in the master equation.

The transformation is made by two methods. The first assumes that the integrand in (2.5) can be expanded in a Taylor series about $\epsilon' = \epsilon$; the second assumes that the kernel $R(\epsilon', \epsilon)$ in (2.5) is separable. The use of these two methods not only makes it possible to deal with a wider range of problems but also permits one to compare results in cases where both methods are applicable.

Taylor Expansion of Integrand

Let us assume that the kernel $R(\epsilon', \epsilon)$ in (2.5) is large only for $|\epsilon' - \epsilon| < 1$ and similarly that the dissociation rate $R(c, \epsilon)$ is appreciable only for ϵ near the dissociation limit δ. Under these conditions, we can anticipate that the solution of (2.5) will be well approximated by that solution of the equation

$$N_e(\epsilon)\frac{\partial X(\epsilon, t)}{\partial t} = \int_{-\infty}^\infty R(\epsilon', \epsilon)[X(\epsilon', t) - X(\epsilon, t)]d\epsilon', \quad (3.1)$$

[56] N. G. van Kampen, Can. J. Phys. **39**, 551 (1961).

which satisfies the boundary condition at $\epsilon = 0$ and δ implicit in (2.5). Expanding $X(\epsilon', t)$ about ϵ, we obtain the partial differential equation

$$N_e\frac{\partial X}{\partial t} = \Delta_1\frac{\partial X}{\partial \epsilon} + \tfrac{1}{2}\Delta_2\frac{\partial^2 X}{\partial \epsilon^2} + O(\Delta_3), \quad (3.2)$$

where

$$\Delta_k(\epsilon) = \int_{-\infty}^\infty R(\epsilon', \epsilon)(\epsilon' - \epsilon)^k d\epsilon' \quad (3.3)$$

is the kth moment of the energy transfer $(\epsilon' - \epsilon)$ with respect to $R(\epsilon', \epsilon)$. We now observe that the symmetry of $R(\epsilon', \epsilon)$ on interchange of ϵ and ϵ' requires that

$$R(\epsilon', \epsilon) = S(\bar\epsilon, |\Delta|), \quad (3.4)$$

where

$$\bar\epsilon = (\epsilon' + \epsilon)/2 \quad (3.5)$$

is the mean of the initial and final energies and

$$\Delta = \epsilon' - \epsilon \quad (3.6)$$

is the energy transfer. If we assume that $S(\bar\epsilon, |\Delta|)$ is sharply peaked at $\Delta = 0$, but varies relatively slowly with $\bar\epsilon$, we may substitute (3.4) into (3.3) and expand about $\bar\epsilon = \epsilon$. This gives

$$\Delta_k(\epsilon) = \int_{-\infty}^\infty \left[S(\epsilon, |\Delta|) + \frac{\partial S}{\partial \bar\epsilon}\bigg|_\epsilon \frac{\Delta}{2} + \cdots \right]\Delta^k d\Delta.$$

It follows that

$$\Delta_1(\epsilon) = \int_0^\infty \frac{\partial S}{\partial \bar\epsilon}\bigg|_\epsilon \Delta^2 d\Delta + O(\Delta^4) \quad (3.7)$$

and

$$\Delta_2(\epsilon) = 2\int_0^\infty S(\epsilon, \Delta)\Delta^2 d\Delta + O(\Delta^4). \quad (3.8)$$

Comparing (3.8) and (3.7) shows that

$$\Delta_1 = \tfrac{1}{2}(\partial\Delta_2/\partial\epsilon) + O(\Delta^4), \quad (3.9)$$

and substituting (3.9) into (3.2), we find to terms of $O(\Delta^4)$

$$N_e\frac{\partial X}{\partial t} = \frac{\partial}{\partial \epsilon}\left(\frac{\Delta_2}{2}\frac{\partial X}{\partial \epsilon}\right). \quad (3.10)$$

This is recognized at once as the ordinary one-dimensional diffusion equation which describes, for example, the flow of heat in a medium of variable heat capacity and conductivity. It displays clearly the diffusion character of the vibrational relaxation under conditions where the average energy transfer in a collision is small.

The boundary conditions necessary to determine $X(\epsilon, t)$ uniquely may be obtained as follows. Integrating (3.10) with respect to ϵ, we find that the flux of molecules crossing the energy surface ϵ is $(\Delta_2/2)\partial X/\partial\epsilon$. Since no molecules can cross the surface $\epsilon = 0$, we

obtain

$$\partial X/\partial \epsilon \,|_0 = 0 \tag{3.11}$$

as one boundary condition. The other may be obtained by matching the flux of molecules crossing the surface $\epsilon = \delta$ to the dissociation rate obtained by integrating the original master equation (2.5). This gives

$$\frac{\Delta_2}{2}\frac{\partial X}{\partial \epsilon}\bigg|_{\delta} = \int_0^{\delta} R(c,\epsilon)\left[\left(\frac{A}{A_e}\right)^2 - X(\epsilon,t)\right]d\epsilon. \tag{3.12}$$

Expanding $X(\epsilon,t)$ about $\epsilon = \delta$, we obtain

$$\frac{\Delta_2}{2}\frac{\partial X}{\partial \epsilon}\bigg|_{\delta} = \Re(\delta)\left[\left(\frac{A}{A_e}\right)^2 - X(\delta,t)\right] + \Gamma_1\frac{\partial X}{\partial \epsilon}\bigg|_{\delta} + O(\Gamma_2), \tag{3.13}$$

where

$$\Re(\delta) = \int_0^{\delta} R(c,\epsilon)d\epsilon \tag{3.14}$$

is the equilibrium dissociation rate and

$$\Gamma_k = \int_0^{\delta} R(c,\epsilon)(\delta-\epsilon)^k d\epsilon \tag{3.15}$$

is the kth moment of $(\delta-\epsilon)$ with respect to $R(c,\epsilon)$. We now observe that

$$R(c,\epsilon) = \int_{\delta}^{\infty} R(\epsilon',\epsilon)d\epsilon', \tag{3.16}$$

so that (3.15) can be written

$$\Gamma_k = \int_0^{\delta}\int_{\delta}^{\infty} R(\epsilon',\epsilon)(\delta-\epsilon)^k d\epsilon' d\epsilon. \tag{3.17}$$

Substituting (3.4) into (3.17) and expanding about $\bar\epsilon = \delta$ gives

$$\Gamma_k = \int_0^{\infty}\int_{-\Delta/2}^{\Delta/2}\left[S(\delta,\Delta) + \frac{\partial S}{\partial \bar\epsilon}\bigg|_{\delta} x + \cdots\right](\tfrac{1}{2}\Delta - x)^k dx d\Delta,$$

and it follows that

$$\Gamma_1 = \frac{1}{2}\int_0^{\infty} S(\delta,\Delta)\Delta^2 d\Delta + O(\Delta^3). \tag{3.18}$$

Comparing (3.18) and (3.8) shows

$$\Gamma_1 = \tfrac{1}{4}\Delta_2(\delta) + O(\Delta^3), \tag{3.19}$$

and substituting (3.19) into (3.13), we find that to terms of $O(\Delta^3)$ our second boundary condition is

$$\tfrac{1}{4}\Delta_2(\delta)(\partial X/\partial \epsilon)\,|_{\delta} = \Re(\delta)[(A/A_e)^2 - X(\delta,t)]. \tag{3.20}$$

This completes the transformation of the master equation (2.5) into an equivalent diffusion equation (3.10) with appropriate boundary conditions (3.11) and (3.20).

The same techniques may also be used to prove an important approximate relation between the "one-way"

equilibrium flux of molecules across the energy surface ϵ,

$$\Re(\epsilon) = \int_{-\infty}^{\epsilon}\int_{\epsilon}^{\infty} R(\epsilon'',\epsilon')d\epsilon''d\epsilon', \tag{3.21}$$

and the first moment of the absolute value of the energy transfer,

$$|\Delta_1|(\epsilon) = \int_{-\infty}^{\infty} R(\epsilon',\epsilon)|\epsilon'-\epsilon|\,d\epsilon'. \tag{3.22}$$

To do so, we substitute (3.4) into (3.21) and (3.22) and expand about ϵ. This gives

$$\Re(\epsilon) = \int_0^{\infty}\int_{-\Delta/2}^{\Delta/2}\left[S(\epsilon,\Delta) + \frac{\partial S}{\partial \bar\epsilon}\bigg|_{\epsilon} x + \cdots\right]dx d\Delta$$

$$= \int_0^{\infty} S(\epsilon,\Delta)\Delta d\Delta + O(\Delta^3) \tag{3.23}$$

and

$$|\Delta_1|(\epsilon) = \int_{-\infty}^{\infty}\left[S(\epsilon,|\Delta|) + \frac{\partial S}{\partial \bar\epsilon}\bigg|_{\epsilon}\frac{\Delta}{2} + \cdots\right]|\Delta|\,d\Delta$$

$$= 2\int_0^{\infty} S(\epsilon,\Delta)\Delta d\Delta + O(\Delta^3). \tag{3.24}$$

Comparing (3.23) and (3.24), we find to terms of $O(\Delta^3)$

$$\Re(\epsilon) = \tfrac{1}{2}|\Delta_1|(\epsilon). \tag{3.25}$$

Since the moments of $R(\epsilon',\epsilon)$ are in general easier to compute (and probably to measure) than the kernel $R(\epsilon',\epsilon)$ itself, the relation (3.25) is extremely useful.

In concluding this section, we should note that while replacing the integral equation (2.5) with an equivalent diffusion equation (3.10) is physically appealing. The principal justification for the procedure is the empirical observation that in situations where $X(\epsilon,t)$ is nicely monotonic, the replacement of the integral equation by a diffusion equation does give good results. Attempts to use more terms in the power series for $X(\epsilon,t)$ and $R(\epsilon',\epsilon)$ are likely to decrease the effectiveness of the technique. Ordinarily, the higher-order counterpart of (3.10) will be very clumsy and give less accurate results. In fact, the full series diverges outside the interval $|\epsilon'-\epsilon| < \delta-\epsilon$ and, for ϵ close to δ, this is most of the range of interest. Therefore, until further clarification of the method is forthcoming, termination of the process at the quadratic stage is advisable.

Separable Kernel

The second method of transforming (2.5) into a differential equation involves the assumption that kernel $R(\epsilon',\epsilon)$ can be separated in the form

$$R(\epsilon',\epsilon) = \begin{cases} r_2(\epsilon')r_1(\epsilon): & \epsilon'>\epsilon \\ r_2(\epsilon)r_1(\epsilon'): & \epsilon>\epsilon' \end{cases}, \tag{3.26}$$

and that the dissociation rate $R(c, \epsilon)$ can be expressed

$$R(c, \epsilon) = r_1(\epsilon) r_c, \qquad (3.27)$$

where r_c is a constant. Substituting (3.26) and (3.27) into (2.8), we obtain

$$\left(N_e \frac{\partial X}{\partial t} + ZX\right) = r_2(\epsilon) \int_0^\epsilon r_1(\epsilon') X(\epsilon') d\epsilon'$$

$$+ r_1(\epsilon)\left[\int_\epsilon^\delta r_2(\epsilon') X(\epsilon') d\epsilon' + r_c\left(\frac{A}{A_e}\right)^2\right], \quad (3.28)$$

where

$$Z(\epsilon) = r_2(\epsilon) \int_0^\epsilon r_1(\epsilon') d\epsilon' + r_1(\epsilon)\left[\int_\epsilon^\delta r_2(\epsilon') d\epsilon' + r_c\left(\frac{A}{A_e}\right)^2\right] \qquad (3.29)$$

is the equilibrium collision rate. Differentiating (3.28) twice with respect to ϵ gives the two additional equations

$$\frac{\partial}{\partial \epsilon}\left(N_e \frac{\partial X}{\partial t} + ZX\right) = \frac{dr_2}{d\epsilon} \int_0^\epsilon r_1(\epsilon') X(\epsilon') d\epsilon'$$

$$+ \frac{dr_1}{d\epsilon}\left[\int_\epsilon^\delta r_2(\epsilon') X(\epsilon') d\epsilon' + r_c\left(\frac{A}{A_e}\right)^2\right] \qquad (3.30)$$

and

$$\frac{\partial^2}{\partial \epsilon^2}\left(N_e \frac{\partial X}{\partial t} + ZX\right) = \frac{d^2 r_2}{d\epsilon^2} \int_0^\epsilon r_1(\epsilon') X(\epsilon') d\epsilon'$$

$$+ \frac{d^2 r_1}{d\epsilon^2}\left[\int_\epsilon^\delta r_2(\epsilon') X(\epsilon') d\epsilon' + r_c\left(\frac{A}{A_e}\right)^2\right] - W\{r_2, r_1\} X, \quad (3.31)$$

where

$$W\{r_2, r_1\} = r_2(dr_1/d\epsilon) - r_1(dr_2/d\epsilon) \qquad (3.32)$$

is the Wronskian of r_2 and r_1. Combining (3.28), (3.30), and (3.31), we find

$$W\{r_2, r_1\} \frac{\partial^2}{\partial \epsilon^2}\left(N_e \frac{\partial X}{\partial t} + ZX\right) = \frac{d^2 r_1}{d\epsilon^2} W\left\{r_2, N_e \frac{\partial X}{\partial t} + ZX\right\}$$

$$- \frac{d^2 r_2}{d\epsilon^2} W\left\{r_1, N_e \frac{\partial X}{\partial t} + ZX\right\} - W^2\{r_2, r_1\} X, \quad (3.33)$$

with the boundary conditions

$$W\{r_1, N_e(\partial X/\partial t) + ZX\}|_0 = 0 \qquad (3.34)$$

and

$$W\{r_2, N_e(\partial X/\partial t) + ZX\}|_\delta = r_c(A/A_e)^2 W\{r_2, r_1\}|_\delta. \qquad (3.35)$$

Since $X = 1$ and $\partial X/\partial t = 0$ at equilibrium, Z satisfies the equation

$$W\{r_2, r_1\} \frac{d^2 Z}{d\epsilon^2} - \left(\frac{d}{d\epsilon} W\{r_2, r_1\}\right) \frac{dZ}{d\epsilon}$$

$$+ W\left\{\frac{dr_2}{d\epsilon}, \frac{dr_1}{d\epsilon}\right\} Z = -W^2\{r_2, r_1\}, \quad (3.36)$$

with the boundary conditions

$$W\{r_1, Z\}|_0 = 0 \qquad (3.37)$$

and

$$W\{r_2, Z\}|_\delta = r_c W\{r_2, r_1\}|_\delta. \qquad (3.38)$$

We therefore obtain, on evaluating the Wronskians in (3.33), (3.34), and (3.35), the equation

$$-\frac{Z}{W}\left[\frac{\partial^2}{\partial \epsilon^2}\left(N_e \frac{\partial X}{\partial t}\right) - \frac{1}{W}\left(\frac{dW}{d\epsilon}\right)\frac{\partial}{\partial \epsilon}\left(N_e \frac{\partial X}{\partial t}\right)\right]$$

$$+ \left(1 - \frac{1}{W}\frac{dZ}{d\epsilon}\right) N_e \frac{\partial X}{\partial t} = \frac{\partial}{\partial \epsilon}\left(\frac{Z^2}{W}\frac{\partial X}{\partial \epsilon}\right), \quad (3.39)$$

with the boundary conditions

$$W\{r_1, N_e(\partial X/\partial t)\} + r_1 Z(\partial X/\partial \epsilon)|_0 = 0, \quad (3.40)$$

and

$$W\left\{r_2, N_e \frac{\partial X}{\partial t}\right\} + r_2 Z \frac{\partial X}{\partial \epsilon}\Big|_\delta = r_c W\left[\left(\frac{A}{A_e}\right)^2 - X\right]\Big|_\delta, \quad (3.41)$$

where we have used W to abbreviate $W\{r_2, r_1\}$. The differential equation (3.39) with its boundary conditions (3.40) and (3.41) is completely equivalent to the original integral equation (2.5) in the case where the kernel is separable in form (3.26). Although it is rather complicated in the general case, it can be simplified considerably in the important special case where the characteristic energy transferred in a collision is small compared to kT. Under this condition, Z is small compared to W and $N_e \partial X/\partial t$ is small compared to Z. As a result, (3.39) becomes approximately

$$N_e \frac{\partial X}{\partial t} = \frac{\partial}{\partial \epsilon}\left(\frac{Z^2}{W}\frac{\partial X}{\partial \epsilon}\right), \qquad (3.42)$$

and the boundary conditions (3.40) and (3.41) become

$$\partial X/\partial \epsilon|_0 = 0 \qquad (3.43)$$

and

$$\frac{\partial X}{\partial \epsilon}\Big|_\delta = \frac{r_c W}{r_2 Z}\left[\left(\frac{A}{A_e}\right)^2 - X\right]\Big|_\delta. \qquad (3.44)$$

Thus, once again, we find that in the limit of small energy transfers, the vibration–dissociation–recombination process can be described by an ordinary diffusion equation.

IV. STEADY-STATE SOLUTIONS

As we anticipate in Sec. 2, the population of vibrational levels after the initial transient has passed can be obtained from a solution of the steady-state dissociation equation (2.9) for the quantum-mechanical model, or (2.23) for the classical model. In this section, we provide exact solutions of (2.9) and, by the method of Sec. 3, approximate solutions of (2.23).

Quantum-Mechanical Model

In treating the dissociation problem using the quantum-mechanical model, we limit ourselves to the

case in which only transitions between adjacent levels are important. The cases where larger steps must be considered are more easily treated using the classical model to be discussed later. In this "ladder-climbing" approximation, (2.9) becomes

$$R(n+1, n)[\chi(n+1)-\chi(n)]$$
$$-(1-\delta_{n0})R(n, n-1)[\chi(n)-\chi(n-1)]=0, \quad (4.1)$$

where we have set $R(c, P-1)=R(P, P-1)$, and δ_{n0} is the Kronecker delta. The boundary conditions are $\chi(0)=1$ and $\chi(P)=0$.

It is now convenient to define $Q(n+1)=\chi(n+1)-\chi(n)$ so that (4.1) becomes

$$R(n+1, n)Q(n+1)-R(n, n-1)Q(n)=0. \quad (4.2)$$

Solving (4.2) by iteration, we obtain

$$Q(n+1)=\frac{R(n, n-1)Q(n)}{R(n+1, n)}=\cdots=\frac{R(1,0)Q(1)}{R(n+1, n)}, \quad (4.3)$$

and

$$\chi(n+1)=\chi(n)+Q(n+1)=\cdots=1+\sum_{k=1}^{n+1}\frac{R(1,0)Q(1)}{R(k, k-1)}. \quad (4.4)$$

Imposing the boundary condition $\chi(P)=0$, we find

$$R(1,0)Q(1)=-\left[\sum_{k=1}^{P}R^{-1}(k, k-1)\right]^{-1}, \quad (4.5)$$

and (4.4) can be written

$$\chi(n)=1-\sum_{k=1}^{n}R^{-1}(k, k-1)\bigg/\sum_{k=1}^{P}R^{-1}(k, k-1). \quad (4.6)$$

Since, for slowly varying transition probabilities $B(k, k-1)$,

$$R(k, k-1)=B(k, k-1)\exp(-\epsilon_{k-1}) \quad (4.7)$$

is a rapidly decreasing function of k, it can be seen that $\chi(n)$ will differ appreciably from unity only in the interval for which $(\epsilon_P-\epsilon_n)\lesssim 1$. Thus, as we anticipated in Sec. II, the distribution of molecules over the vibrational levels is "almost Boltzmann" except near the dissociation limit where it is depressed.

The steady-state dissociation rate constant obtained by substituting (4.6) into (2.17) is

$$k_d=\left[M_e\sum_{k=1}^{P}R^{-1}(k, k-1)\right]^{-1}, \quad (4.8)$$

and the corresponding equilibrium rate constant obtained from (2.20) is

$$k_{de}=R(P, P-1)/M_e. \quad (4.9)$$

These results are substantially identical to those obtained by Stupochenko and Osipov.[17]

Quantized Morse Oscillator

We now consider the application of the above results to the case of a nonrotating quantized Morse oscillator. The potential energy of such an oscillator is given by

$$V_M(r)=D\{1-\exp[-\beta(r-r_e)]\}^2, \quad (4.10)$$

and the vibrational transition rate may be approximated by[1]

$$R(n, n-1)=Z_0a_nf_2(\omega_n\tau)\exp(-\epsilon_n), \quad (4.11)$$

where

$$Z_0=\sigma\bar{c}(1-e^{-\theta})A_3M_e \quad (4.12)$$

is the collision rate,

$$a_n\approx(2\mu_3/\theta\mu_{12})2Pn/(2P-n) \quad (4.13)$$

is the resonance transition probability for a Morse oscillator,[57]

$$f_2(x)=x^2\int_0^{\infty}e^{-y}\operatorname{csch}^2(xy^{-\frac{1}{3}})dy \quad (4.14)$$

is the adiabaticity factor,

$$\omega_n\approx kT(\epsilon_n-\epsilon_{n-1})/\hbar=\omega_0(1-n/P) \quad (4.15)$$

is the angular frequency of the transition,

$$\epsilon_n\approx\theta(n+\tfrac{1}{2})[1-(n+\tfrac{1}{2})/2P] \quad (4.16)$$

is the energy of the upper level, $\theta=\hbar\omega_0/kT$ is the ground-state level spacing divided by kT, σ is the kinetic cross section, $\bar{c}=(8kT/\pi\mu_3)^{\frac{1}{2}}$ is the mean speed for collisions of molecules and background atoms, M_e is the equilibrium concentration of molecules, A_3 is the concentration of background atoms, μ_3 is the reduced mass for the collision, μ_{12} is the reduced mass of the molecules, $\tau=(\pi L)(\mu_3/2kT)^{\frac{1}{2}}$ is the effective collision time for an exponential interaction potential $V_3=V_0\exp(-r/L)$, $P\approx 2D/\hbar\omega_0$ is the number of levels in the potential well, $\omega_0=\beta(2D/\mu_{12})^{\frac{1}{2}}$ and other quantities have been previously defined. Note that (4.10) exhibits explicitly the important dependence of $R(n, n-1)$ on the adiabaticity factor, $f_2(\omega_n\tau)$, which may change by many orders of magnitude as n approaches P due to the decrease in the level spacing near the dissociation limit.

The adiabaticity factor (4.13) may be evaluated[58] by the method of steepest descent and is found to be

$$f_2(x)\approx 8(\pi/3)^{\frac{1}{2}}x^{7/3}\exp(-3x^{\frac{2}{3}}), \quad (4.17)$$

where $x\gg 1$. By numerical integration and curve fitting,

[57] R. Herman and K. E. Shuler, J. Chem. Phys. 21, 373 (1953).
[58] (a) R. N. Schwartz and K. R. Herzfeld, J. Chem. Phys. 22, 767 (1954); (b) R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, ibid. 20, 1591 (1952).

we have found a more convenient expression,

$$f_2(x) \approx (\tfrac{1}{2})[3 - \exp(-2x/3)]\exp(-2x/3), \quad (4.18)$$

which is equally accurate ($\pm 20\%$) for $0 \leq x \leq 20$, and bridges the gap between the cases of impulsive and adiabatic energy exchange. We, therefore, use (4.18) instead of (4.17) in our calculations.

Using (4.18), we can now estimate the partial sum,

$$S_n = \sum_{k=1}^{n} R^{-1}(k, k-1), \quad (4.19)$$

appearing in our expression (4.6) for the population distribution. To do this, we first replace the summation by an integral so that

$$S_n \approx \frac{2}{Z_0} \int_0^n \exp\left\{\tfrac{2}{3}\omega_0\tau(1-k/P) + \theta(k+\tfrac{1}{2})\left[1 - \frac{(k+\tfrac{1}{2})}{2P}\right]\right\} dk \Big/ a_k[3 - \exp\{\tfrac{2}{3}\omega_0\tau(1-k/P)\}], \quad (4.20)$$

and observe that the numerator of the integrand has a strong maximum at

$$k \approx n^* = P - P(\gamma/\delta)^{\frac{1}{2}}, \quad (4.21)$$

where

$$\gamma = (\tfrac{1}{3}\pi\beta L)^2 \mu_3/\mu_{12} \quad (4.22)$$

is a parameter which determines the "softness" of the collisions. In particular, the adiabaticity parameter, $\omega\tau$, is related to γ by the equation

$$\omega_n\tau = 3[\gamma(\delta - \epsilon_n)]^{\frac{1}{2}}, \quad (4.23)$$

which shows that as γ increases, the collisions become softer (more nearly adiabatic). For a hard-sphere interaction, the value of γ is zero.

Evaluating the denominator in (4.20) at $k = n^*$ and the remaining integral by completing the square, we obtain

$$S_n \approx \left(\frac{2\pi P}{\theta}\right)^{\frac{1}{2}} \left(\frac{2\exp\{\delta + \gamma\}}{Z_0 a^*[3 - \exp\{-2\gamma\}]}\right) \text{erf}\left\{\left(\frac{\theta}{P}\right)^{\frac{1}{2}}(n - n^*)\right\}, \quad (4.24)$$

where

$$\text{erf}\{t\} = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^{t} \exp\tfrac{1}{2}(-x^2)dx \quad (4.25)$$

is the error function. Note that in evaluating (4.20), we have assumed $P(\gamma/\delta)^{\frac{1}{2}} > 1$ and extending the range of integration to $-\infty$. This restricts the range of validity of (4.24) to $\gamma P^2 > \delta > (1+\gamma^{\frac{1}{2}})^2$, which includes most of the situations of current interest. Although both approximations have been made as a mathematical convenience and can be removed, there is little point in doing so since for δ greater than γP^2, n^* lies above the last bound state of the molecule which is physically unacceptable, and for $\delta < [1+\gamma^{\frac{1}{2}}]^2$, the steady-state approximation is no longer valid.

Substituting (4.24) into (4.6), we find

$$\chi(n) = 1 - \text{erf}\{(\theta/P)^{\frac{1}{2}}(n - n^*)\}/\text{erf}\{(2\gamma)^{\frac{1}{2}}\}, \quad (4.26a)$$

or in terms of ϵ_n,

$$\chi(n) = 1 - \text{erf}\{(2\gamma)^{\frac{1}{2}} - [2(\delta - \epsilon_n)]^{\frac{1}{2}}\}/\text{erf}\{(2\gamma)^{\frac{1}{2}}\}. \quad (4.26b)$$

A plot of $\chi(n)$ as a function of $(\delta - \epsilon_n)$ for several values of γ is shown in Fig. 1(a). The maximum value of $d\chi(n)/dn$ occurs at $n = n^*$, and this in effect locates the position of a "bottleneck" in the excitation process at $\delta - \epsilon^* = \gamma$. Below the "bottleneck," the vibrational levels are populated in accord with a Boltzmann distribution, while above the "bottleneck" the levels are depleted due to drainage to the continuum. In the case of recombination, the situation is of course reversed, and the population is proportional to $[1 - \chi(n)]$ as shown by (2.10).
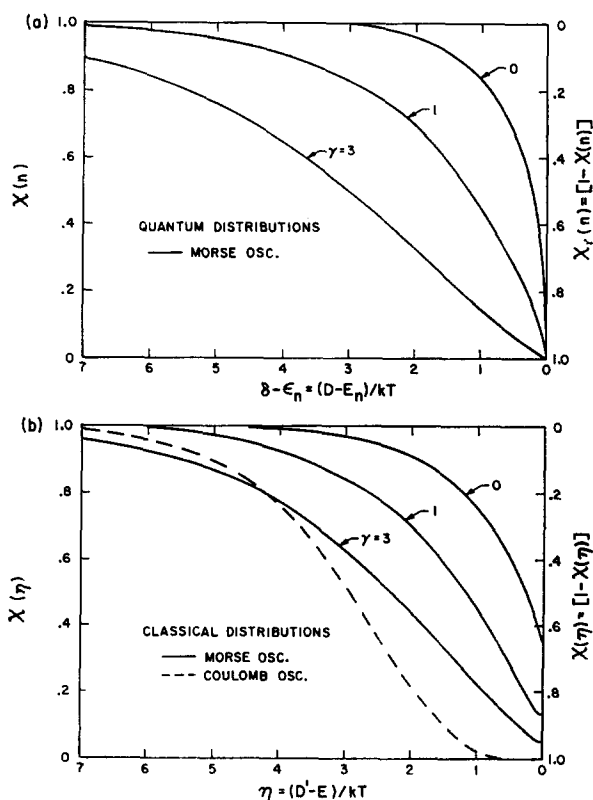

FIG. 1. Steady-state distribution functions for: (a) a quantized Morse oscillator and (b) classical Morse and Coulomb oscillators. The left scale refers to dissociation and the right to recombination. The parameter γ is defined by (4.22).

The steady-state dissociation rate constant obtained by substituting (4.24), into (4.8) is

$$k_d = \sigma \bar{c} A_3 e^{-\delta} (1 - e^{-\theta}) (2P/\pi\theta)^{\frac{1}{2}} G, \qquad (4.27)$$

where

$$G = \left(\frac{\mu_3}{\mu_{12}}\right) \left(\frac{1 - (\gamma/\delta)^{\frac{1}{2}}}{1 + (\gamma/\delta)^{\frac{1}{2}}}\right) \frac{(3 - \exp\{-2\gamma\}) \exp\{-\gamma\}}{\text{erf}\{(2\gamma)^{\frac{1}{2}}\}}. \qquad (4.28)$$

Dividing (4.27) by the equilibrium constant

$$K_e = (g^2/g_{12}) (\beta/4\pi r_e^2) (2P/\pi\theta)^{\frac{1}{2}} (1 - e^{-\theta}) e^{-\delta}, \qquad (4.29)$$

we obtain the corresponding steady-state recombination rate constant

$$k_r = (g_{12}/g^2) \sigma \bar{c} A_3 (4\pi r_e^2/\beta) G = k_3 G, \qquad (4.30)$$

where g and g_{12} are, respectively, the electronic degeneracies of the free atoms and molecule. The factor k_3 defined in (4.30) is just the ordinary kinetic theory three-body collision rate constant. It is well known to give the right order of magnitude for the recombination rate, but contains almost no temperature dependence due to the fact that the positive temperature coefficient of the thermal speed $\bar{c}$ is nearly cancelled by the negative temperature coefficient of the cross section σ. This deficiency, however, is corrected by the factor G, which exhibits the appropriate negative temperature dependence in the range $\delta > (1+\gamma^{\frac{1}{2}})^2$ where the steady-state approximation is valid.

Models similar to that discussed above have been investigated previously, both numerically[11,20] and analytically,[7,14,17] with generally similar results. The principal difference between the present work and previous analytical work is that we have included a detailed specification of the manner in which the transition probabilities vary with the energy of the oscillator. This leads to somewhat different conclusions about the location of the "bottleneck" and the temperature and mass dependence of the rate constant, but has little effect on its magnitude.

Although the Morse oscillator model disposes of all the objections raised in the case of the truncated harmonic oscillator[16] and is promising in terms of comparison with experiment, it is still open to criticism on the grounds that it only takes into account transitions between adjacent states. For this approximation to be valid, the single-step transition probability, $a_n f_2(\omega_n \tau)$, evaluated at the "bottleneck" must be appreciably less than unity. Since $\omega_n \tau = 3\gamma$ at the "bottleneck," this leads to the condition

$$\delta > (\mu_3/\mu_{12}) P^2 \exp\{-2\gamma\}. \qquad (4.31)$$

Using reasonable values for the parameters, i.e., $P > 15$, $\gamma \sim \mu_3/\mu_{12} \sim 1$, (4.31) shows that the one-step approximation is only valid at temperatures much lower than those usually of interest for dissociation or recombination and, thus, the single-step quantum model cannot

be regarded as satisfactory for describing these processes and a multiple-step classical model must be considered.

Classical Model

For the classical model, the steady-state population distribution may be obtained by integrating either (3.10) or (3.42) with $\partial X/\partial t = 0$ and replacing the boundary condition $\partial X/\partial \epsilon |_0 = 0$ by $\chi(0) = 1$. As is well known, the latter step is necessary to obtain nonzero solutions of the steady-state equation. Note that in the steady-state approximation, Eq. (3.42) is exact for a separable kernel.

The general solution of (3.10) is

$$\chi_1(\epsilon) = 1 - \left(\int_0^\epsilon \frac{dx}{\Delta_2}\right) \Big/ \left(\int_0^\delta \frac{dx}{\Delta_2} + C\right), \qquad (4.32)$$

and imposing the boundary condition

$$-d\chi/d\epsilon |_\delta = 4\mathfrak{R}(\delta)\chi(\delta)/\Delta_2(\delta) \qquad (4.33)$$

obtained from (3.20) by setting $A(t) = 0$, we find

$$\chi_1(\epsilon) = 1 - \left[\int_0^\epsilon \frac{dx}{\Delta_2}\right] \Big/ \left[\int_0^\delta \frac{dx}{\Delta_2} + \frac{1}{4\mathfrak{R}(\delta)}\right]. \qquad (4.34)$$

The corresponding steady-state dissociation rate constant obtained by substituting (4.34) into (2.25) and using (3.12) with $A(t) = 0$ is

$$k_{d1} = \left\{2M_e \left[\int_0^\delta \frac{dx}{\Delta_2} + \frac{1}{4\mathfrak{R}(\delta)}\right]\right\}^{-1}. \qquad (4.35)$$

The same procedure may be applied in solving (3.42), imposing in this case the boundary condition

$$-d\chi/d\epsilon |_\delta = r_c W(\delta)\chi(\delta)/r_2(\delta) Z(\delta) \qquad (4.36)$$

obtained from (3.44) with $A(t) = 0$. The result for the steady-state distribution may be written

$$\chi_2(\epsilon) = 1 - \left[\int_0^\epsilon \frac{W dx}{Z^2}\right] \Big/ \left[\int_0^\delta \frac{W dx}{Z^2} + \frac{r_2(\delta)}{r_c Z(\delta)}\right], \qquad (4.37)$$

and the steady-state rate constant is

$$k_{d2} = \left\{M_e \left[\int_0^\delta \frac{W dx}{Z^2} + \frac{r_2(\delta)}{r_c Z(\delta)}\right]\right\}^{-1}. \qquad (4.38)$$

For future reference we may note that the equilibrium rate constant obtained by setting $\chi(\epsilon) = 1$ in (2.25) is

$$k_{de} = \mathfrak{R}(\delta)/M_e. \qquad (4.39)$$

We now use the above results to find the steady-state population distributions and dissociation rate constants for classical harmonic, Morse, and Coulomb oscillators.

Classical Harmonic Oscillator

It is interesting to compare the solutions of (3.10) and (3.42) for the simple separable kernel

$$R(\epsilon', \epsilon) = \begin{cases} \exp[-\alpha(\epsilon' - \epsilon) - \epsilon'] : & \epsilon' > \epsilon \\ \exp[-\alpha(\epsilon - \epsilon') - \epsilon] : & \epsilon > \epsilon' \end{cases}, \qquad (4.40)$$

and dissociation rate

$$R(c, \epsilon) = \int_\delta^\infty R(\epsilon', \epsilon)d\epsilon' = \frac{\exp[\alpha\epsilon - (\alpha+1)\delta]}{(\alpha+1)}. \quad (4.41)$$

From a physical point of view, this kernel gives a reasonable description of a truncated harmonic oscillator near the dissociation limit where the variation in the pre-exponential factor with energy can be neglected.

Comparing (4.40) and (4.41) with (3.26) and (3.27), we find

$$r_1(\epsilon) = e^{\alpha\epsilon}, \quad (4.42a)$$

$$r_2(\epsilon) = \exp[-(\alpha+1)\epsilon], \quad (4.42b)$$

and

$$r_c = \exp[-(\alpha+1)\delta]/(\alpha+1). \quad (4.42c)$$

It follows from (3.3) and (3.14) that for $\delta \gg 1$

$$\Delta_2(\epsilon) = e^{-\epsilon} 2[\alpha^3 + (\alpha+1)^3]/\alpha^3(\alpha+1)^3, \quad (4.43a)$$

$$\mathfrak{R}(\delta) = e^{-\delta}/\alpha(\alpha+1), \quad (4.43b)$$

and from (3.32) and (3.29) that

$$W(\epsilon) = e^{-\epsilon}(2\alpha+1), \quad (4.44a)$$

$$Z(\epsilon) = e^{-\epsilon}[2\alpha+1 - (\alpha+1)e^{-\alpha\epsilon}]/\alpha(\alpha+1). \quad (4.44b)$$

Substituting (4.44) into (4.37) and (4.38) and noting that the equilibrium distribution implied by (4.40) is $N_e(\epsilon) = e^{-\epsilon}$ so that $M_e \approx 1$, we obtain for $\epsilon \gg \alpha^{-1}$ the exact specific distribution

$$\chi_2(\epsilon) = 1 - \exp[-(\delta-\epsilon)]\alpha/(\alpha+1), \quad (4.45)$$

and steady-state dissociation rate constant

$$k_{d2} = e^{-\delta}(2\alpha+1)/\alpha(\alpha+1)^3. \quad (4.46)$$

The corresponding approximate results obtained from (4.43), (4.34), and (4.35) are

$$\chi_1(\epsilon) = 1 - \exp[-(\delta-\epsilon)][\alpha/(\alpha+1)](1+\tfrac{1}{2}\alpha^2 \cdots), \quad (4.47)$$

and

$$k_{d1} = e^{-\delta}[(2\alpha+1)/\alpha(\alpha+1)^3](1+\tfrac{3}{2}\alpha^2 + \cdots). \quad (4.48)$$

Thus, to terms of order α^{-2} the approximate equation (3.10), which is applicable to any narrow kernel, gives results in agreement with the exact results of Eq. (3.42) for a separable kernel. The condition $\alpha^{-2} \ll 1$ means physically that the characteristic energy transferred in a collision must be somewhat less than the thermal energy kT of the background atoms. It can be seen later that this is expected to be the case.

It should be noted that if we had used the integral equation itself, rather than (3.20) to obtain the boundary condition at $\epsilon = \delta$, the approximate equation would also have given the exact answer. This is because, for the particular separable kernel (4.40) employed in the analysis, Δ_2 is proportional to Z^2/W, so

that the use of the exact boundary condition leads to the exact answer.

Classical Morse Oscillator

The vibrational transition rates near the dissociation limit of a rotating Morse oscillator have been investigated by Woznick[29] and Keck[30] using numerical trajectory calculations. The calculations were made for H_2, O_2, and I_2 in Ar and O_2 in Xe for values of δ equal to 10 and 100. They covered the energy range from 0 to $3\,kT$ below the dissociation limits with statistical errors varying from $\pm 10\%$ at the dissociation limit to $\pm 20\%$ at $3\,kT$ below. Within the statistical errors, the "one-way" equilibrium flux of molecules across a surface a fixed energy $\eta = \delta' - \epsilon$ below the top of the rotational barrier is given by

$$\mathfrak{R}(\eta) = Z_0 a(\eta) f_1(\omega\tau) \exp(-\delta+\eta), \quad (4.49)$$

where

$$a(\eta) = \theta^{-1}\left(\frac{\mu_3\delta}{\mu_{12}\pi}\right)^{\frac{1}{2}}\left[\frac{1-(\eta/\delta)^{\frac{1}{2}}}{1+(\eta/\delta)^{\frac{1}{2}}}\right]\left(\frac{z_2}{r_e}\right)^2$$

$$\times[1-\exp(-b_m)]\beta(z_2-z_1)\phi \quad (4.50)$$

is the classical transition probability for a rotating Morse oscillator,

$$f_1(x) = 2\pi^{-\frac{1}{2}}x\int_0^\infty e^{-y}\operatorname{csch}(xy^{-\frac{1}{2}})dy \approx \tfrac{1}{3}[4 - \exp(-4x/9)]$$

$$\times \exp(-4x/9) \quad (4.51)$$

is the appropriate form of the adiabaticity factor in the classical case,

$$\omega \approx \omega_0(\eta/\delta)^{\frac{1}{2}} \quad (4.52)$$

is the effective frequency of a rotating Morse oscillator, z_2 is the most probable position of the rotational barrier, z_1 is the corresponding inner turning point, ϕ is a slowly varying geometrical factor having a value near $\tfrac{1}{3}$, $b_m = (\delta' - \delta)_m$ is the height of the rotational barrier in units of kT at which the minimum in the effective potential disappears and other quantities are as previously defined.

It was also found within the statistical errors that

$$\Delta_2(\eta) = 2\mathfrak{R}(\eta) = |\Delta_1|(\eta). \quad (4.53)$$

It may be noted that if the transition kernel $R(\epsilon', \epsilon)$ is assumed to fall off exponentially with $|\epsilon'-\epsilon|$, then (4.53) implies a value of $kT/2$ for the characteristic energy transfer in a collision. Thus, the diffusion equation (3.10) should be a reasonable approximation.

We may now evaluate the integral,

$$S(\eta) = \int_\eta^{\delta'} \frac{dx}{\Delta_2} = \int_0^\epsilon \frac{dx}{\Delta_2}, \quad (4.54)$$

appearing in our expression (4.32) for the steady-state distribution. Using (4.49) and (4.53), we find

$$S(\eta) = \frac{3}{2Z_0} \int_{\eta}^{\delta'} \frac{\exp\{\delta - x + 4(\gamma x)^{\frac{1}{2}}/3\} dx}{a(x)[4 - \exp\{-4(\gamma x)^{\frac{1}{2}}/3\}]}. \quad (4.55)$$

The numerator in this integral has a maximum at $x = 4\gamma/9$. Evaluating the denominator at the maximum and the remaining integral exactly, we obtain

$$S(\eta) = \frac{3 \exp\{\delta + 4\gamma/9\} H_\gamma \{(8\gamma/9)^{\frac{1}{2}} - (2\eta)^{\frac{1}{2}}\}}{2Z_0 a(4\gamma/9)[4 - \exp\{-8\gamma/9\}]}, \quad (4.56)$$

where

$$H_\gamma\{t\} = (4/3)(\pi\gamma)^{\frac{1}{2}} \operatorname{erf}\{t\} + \exp\{-t^2/2\}, \quad (4.57)$$

and erf $\{t\}$ is the error function as defined by (4.25). The range of validity of (4.56) is $\delta > [1 + (4\gamma/9)^{\frac{1}{2}}]^2$, a condition which is also required by the steady-state approximation. Substituting (4.56) into (4.34), and noting that $\eta = 0$ corresponds to the dissociation limit, we obtain for the specific distribution during dissociation

$$\chi(\eta) = 1 - \frac{H_\gamma\{(\frac{8}{9}\gamma)^{\frac{1}{2}} - (2\eta)^{\frac{1}{2}}\}}{H_\gamma\{(\frac{8}{9}\gamma)^{\frac{1}{2}}\}[1 + \frac{1}{4}\Re(0) S(0)]}, \quad (4.58)$$

where from (4.49) and (4.56), we find

$$2\Re(0) S(0) = \left(\frac{3H_\gamma\{(\frac{8}{9}\gamma)^{\frac{1}{2}}\}}{4 - \exp\{-\frac{8}{9}\gamma\}}\right)\left(\frac{1 + (4\gamma/9\delta)^{\frac{1}{2}}}{1 - (4\gamma/9\delta)^{\frac{1}{2}}}\right). \quad (4.59)$$

In the limit of impulsive collisions $\gamma \to 0$ and (4.58) simplifies to

$$\chi^I(\eta) = 1 - \frac{2}{3} \exp - (\eta), \quad (4.60)$$

which is nearly identical to the result (4.47) for a value of $\alpha = 2$. This is to be expected since for $\gamma \to 0$ our treatment of the Morse oscillator reduces to that for the truncated harmonic oscillator. A plot of $\chi(\eta)$ for several values of γ is shown in Fig. 1(b).

The corresponding steady-state dissociation rate constant obtained using (4.35) and (4.39) is

$$k_d = k_{de}/[2\Re(0) S(0) + \frac{1}{2}], \quad (4.61)$$

where

$$k_{de} = \sigma \bar{c} A_3 (1 - e^{-\theta}) a(0) e^{-\delta} \quad (4.62)$$

is the equilibrium rate constant.

Dividing (4.61) by the equilibrium constant (4.29), we obtain the steady-state recombination rate constant

$$k_r = k_{re}/[2\Re(0) S(0) + \frac{1}{2}], \quad (4.63)$$

where

$$k_{re} = 4\pi^{\frac{3}{2}}(g_{12}/g^2)(\omega_0/\beta) a^2 z_2^2 (z_2 - z_1) \phi[1 - \exp(-b_m)]\delta^{-\frac{1}{2}} \quad (4.64)$$

is the "barrier" rate constant[13] for a repulsive third body; k_{re} may be evaluated with the aid of curves given in the Appendix and molecular constants tabulated by Herzberg.[59]

---

[59] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).
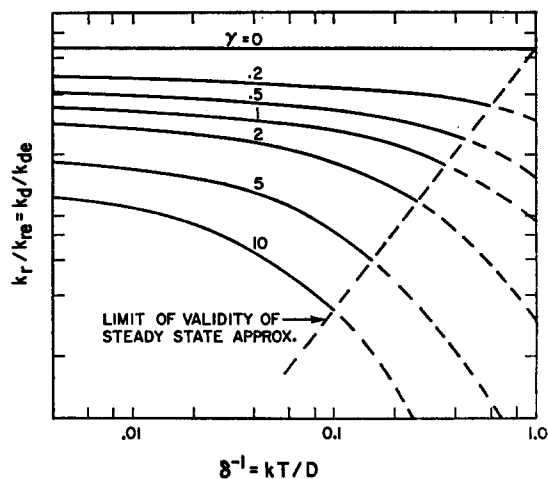

FIG. 2. Ratio of steady state to equilibrium rate constants as a function of kT/D for various values of the parameter γ defined by (4.22).

Equations (4.61) and (4.63) show that the effect of a non-Boltzmann distribution in the states near the dissociation limit is to depress the equilibrium rate constants by the factor $[2R(0) S(0) + \frac{1}{2}]^{-1}$. A plot of this factor as a function of δ for several values of γ is shown in Fig. 2, and it can be seen that the temperature dependence is at least qualitatively correct to explain the experimentally observed negative temperature dependence of the recombination rate.

A quantitative comparison of the theoretical and experimental recombination rate constants for a variety of atoms recombining in excess argon at high temperatures is shown in Table I. It can be seen that the theory reproduces the general trend of the data but predicts rate constants which are somewhat too large for the light atoms and a negative temperature dependence, which is too weak for the heavy atoms. The most probable cause of these discrepancies on the theoretical side is the approximate nature of the potential[60] used to represent the interaction of the third body and the molecule. In particular, the theoretical rate constant is quite sensitive to the range L of the interaction potential and the changes necessary to bring the theory into agreement with the experiments are less than a factor of 2 in all cases. However, in view of the discrepancies of a factor of 2 or 3 between the data of the various workers and the distinct possibility of further systematic errors in shock-tube measurements of this type, such changes are of doubtful significance. Unfortunately, a meaningful comparison with the low-temperature data cannot be made at this time because the attractive van der Waals force which is important at low temperatures has not been taken into account in the theory. Work on this problem is in progress.

A treatment of this problem which involves very much the same basic physical assumptions has been

---

[60] E. A. Mason and J. T. Vanderslice, J. Chem. Phys. **28**, 432 (1958).

TABLE I. Comparison of theoretical recombination rate constants with the available shock-tube data for various homonuclear molecules and inert gases. The rate constants have been reduced to the form $k_r = A(D/20\ kT)^n \times 10^{14}$ cc²/mole·sec and the coefficients A and n are given in Columns 5–8. Columns 1 and 2 identify the molecule and inert atom. Column 3 gives the dissociation temperature of the molecule. Column 4 shows the temperature range covered by the experiments, and Column 9 gives the experimental reference. It should be noted that the values of n_{exptl} given in Column 6 are those determined locally and have a very large uncertainty. In particular, the values in parentheses were either assumed or determined from data covering a temperature range of less than a factor of 1.5. The Cl_2 rate measured by Hiraoka and Hardwick[48] seems to be somewhat out of line with other experimental data. Possible reasons for this are discussed by Jacobs and Giedt.[47]

Molecule	Atom	D/k (°K)	Range (kT/D)	A_{exptl}	$A_{theoret}$	n_{exptl}	$n_{theoret}$	Ref.
H_2	Ar	52 000	0.05–0.09	2.3	25	1	0.9	34
H_2	Ar	52 000	0.05–0.09	2.9	25	1	0.9	35
H_2	Ar	52 000	0.05–0.09	5.8	25	1	0.9	36
H_2	Kr	52 000	0.05–0.09	5.8	25	1	0.9	36
H_2	Xe	52 000	0.05–0.09	5.8	25	1	0.9	36
H_2	Xe	52 000	0.05–0.09	4.5	25	0	0.9	37
D_2	Ar	52 000	0.05–0.09	2.9	18	1	0.9	34
D_2	Ar	52 000	0.05–0.09	2.7	18	1	0.9	35
D_2	Kr	52 000	0.05–0.09	2.7	18	1	0.9	35
N_2	Ne	115 000	0.05–0.08	4.7	2	0.5	0.5	38
	Ar	115 000	0.05–0.09	2.3	2	0.5	0.5	38
	Ar	115 000	0.05–0.08	1.6	2	0	0.5	39
O_2	Ar	60 000	0.03–0.3	0.22	0.8	0	0.5	40
O_2	Ar	60 000	0.06–0.11	0.6	0.8	$\frac{1}{2}$–1	0.5	43
O_2	Ar	60 000	0.05–0.08	0.5	0.8	0	0.5	44
O_2	Ar	60 000	0.07–0.08	0.17	0.8	(1)	0.5	41
O_2	Kr	60 000	0.06–0.09	0.5	0.8	(1)	0.5	41
O_2	Xe	60 000	0.05–0.1	1.5	0.8	$\frac{1}{2}$–2	0.5	42
F_2	Ar	18 300	0.06–0.09	0.16	0.5	2	0.5	46
Cl_2	Ar	28 600	0.06–0.09	3.2	3	1.6	0.5	47
Cl_2	Ar	28 600	0.05–0.1	30	3	1	0.5	48
Br_2	He	22 700	0.07–0.08	8.9	4	(5/2)	0.3	51
Br_2	Ar	22 700	0.05	8.2	4	⋯	0.3	50
Br_2	Ar	22 700	0.06–0.08	7.5	4	(2)	0.3	51
Br_2	Ar	22 700	0.06–0.08	7.0	4	(2)	0.3	52
Br_2	Ar	22 700	0.06–0.08	3.8	4	($\frac{1}{2}$)	0.3	53
I_2	He	17 800	0.06–0.1	7.5	4	2.8	0.3	54
I_2	Ar	17 800	0.06–0.09	9.1	4	1.8	0.3	54

given by Rice.[3,10] The most important difference between Rice's treatment and ours is that Rice has made the approximation that the energy is transferred in discrete amounts and assumed that the collisions are impulsive, whereas we have treated the problem continuously and included an adiabaticity factor. This leads to somewhat different predictions about the dependence of the rate constant on temperature and species.

Classical Coulomb Oscillator

The de-excitation of a Coulomb oscillator by electron impact has been investigated classically by Makin and Keck,[61] who obtained an expression for the one-way equilibrium flux of excited atoms across a surface an

---

energy η below the dissociation limit of the form

$$\Re(\eta) = \Re_T \exp(8\eta/5)/(\eta)^4, \quad (4.65)$$

where

$$\Re_T = \tfrac{3}{4}\bar{c}_e(e^2/kT)^5 n\, n_e^2. \quad (4.66)$$

If we make the tentative assumption that the second moment of the energy transfer, $\Delta_2(\eta)$, is proportional to $\Re(\eta)$ as in the case of the Morse oscillator, then the specific distribution during steady-state ionization obtained from (4.34) is

$$\chi(\eta) = 1 - \exp-\tfrac{8}{5}\eta \sum_{k=0}^{4} \frac{1}{k!}(\tfrac{8}{5}\eta)^k. \quad (4.67)$$

Note that in obtaining (4.67), we have set $[4\Re(\delta)]^{-1}$ in (4.34) equal to zero, which is appropriate for a Coulomb oscillator since the "one-way" equilibrium

---

[61] B. Makin and J. C. Keck, Phys. Rev. Letters **11**, 281 (1963).

flux at the dissociation limit is infinite due to the infinite range of the force. A plot of $\chi(\eta)$ is shown in Fig. 1(b).

The corresponding distribution during recombination is $\chi_r(\eta) = 1 - \chi(\eta)$ and a curve of this distribution is shown in Fig. 3 as a function of η. Also plotted in the figure is the population distribution for a recombining He+ plasma deduced from the measurements of Hinnov and Herschberg.[55] Considering the arbitary nature of our assumption that $\Delta_2(\eta) \propto \mathcal{R}(\eta)$, the agreement is remarkably good and suggests that there may be some basis for the assumption. A numerical investigation of this question similar to that carried out for the Morse oscillator is currently in progress.

To calculate the ionization or recombination rate, the constant of proportionality between $\Delta_2(\eta)$ and $\mathcal{R}(\eta)$ must be known and, since the situation is quite uncertain, we defer such calculations until the necessary information becomes available.

V. CONCLUDING REMARKS

In this paper we have investigated the coupled vibration–dissociation–recombination of a dilute mixture of diatomic molecules in an inert gas. Both quantum and classical models of the process have been examined, and it is concluded that the classical model is a better physical approximation than the frequently used one-step quantum model. The reason for this is that near the dissociation limit, transitions between states are so rapid that the perturbation treatment used to obtain the quantum-mechanical transition probabilities breaks down completely. On the other hand, this is just the situation in which the classical approximation is expected to be valid.

In treating the problem classically, we have reduced the master equation governing the population distribution to an equivalent diffusion equation with variable coefficients. This equation is the analog of the thermal diffusion equation with an effective heat capacity proportional to the equilibrium population and an effective conductivity proportional to the second moment of the energy transfer in the collisions. The equation has been solved in the steady-state approximation for Morse oscillators interacting with repulsive third bodies. The effective conductivities (second moments) have been obtained from numerical trajectory calculations. The results show that the main effect of nonequilibrium in the vibrational degree of freedom during dissociation or recombination is to depress the reaction rate constants below the values that would be computed for a Boltzmann distribution by an amount which increases as the collisions become more adiabatic (softer). A small additional negative temperature coefficient is also introduced but it is appreciable only for quite adiabatic collisions.

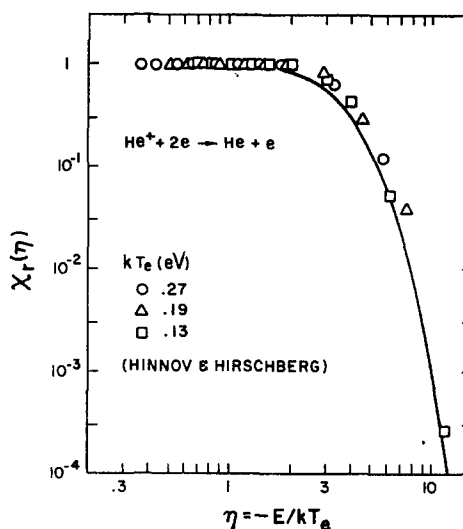A comparison of the results with the available experimental data on the dissociation of homonuclear di-

FIG. 3. Comparison of calculated steady-state distribution with experimental data of Hinnov and Hirschberg[55] for a recombining helium plasma.

atomic molecules by inert gases at high temperatures shows reasonable agreement for a wide range of species. A meaningful comparison with low-temperature data on recombination cannot be made at this time due to neglect of the attractive van der Waals interaction in the potentials used.

The theory may also be used to describe the ionization and recombination of atoms by electron impact. Unfortunately, there are no reliable data on the moments of the energy transfer for electronic excitation which properly include the effects of adiabatic collisions. However, by assuming that the first and second moment are proportional, it is possible to compute the population distribution during recombination and a comparison with the experimental results of Hinnov and Hirshberg[55] for a recombining He+ plasma shows surprisingly good agreement.

To conclude, we feel that the agreement between theory and experiment is sufficiently good to establish that the classical diffusion treatment discussed above is a reasonably good physical approximation. In this connection, it may be noted that rotation has been effectively included in the theory by using effective conductivities from numerical trajectory analyses which refer to an energy coordinate measured from the top of the rotational barrier. An alternative approach which is currently being developed is to generalize the diffusion equation to more dimensions and consider the simultaneous diffusion of both energy and angular momentum. Further problems which should also be investigated include: (1) the effect of attractive interactions between the molecules and third bodies, (2) the failure of the steady-state approximation at high temperatures, (3) the transient behavior at early times, (4) the nonlinear transient vibration–recombination process, and last but not least, (5) the use of the

theory to obtain information about the interaction potential.

ACKNOWLEDGMENTS

The authors would like to thank A. Lande, who participated in the early phases of this work, for many stimulating discussions, and B. Woznick, M. Camac, and N. Snider for comments on the manuscript.

APPENDIX: COMPUTATION OF BARRIER RATE CONSTANT

For most cases of current interest, the "barrier" rate constant (4.64) for a Morse oscillator may be determined from the curves in Figs. 4(a) and 4(b) obtained from data in Refs. 13 and 29. The combination of factors given in Fig. 4(b) is a function only of the temperature and molecular parameters, while the combination given in Fig. 4(a) involves an additional dependence on the effective collision radius a. The molecular parameters required have been tabulated by Herzberg.[59] The collision radius is defined as the radius at which $(dV_3/dr)\exp(-V_3/kT)$ has a maximum, where V_3 is the interaction potential for an atom of the molecule and the "third body." For an exponential interaction of the Mason–Vanderslice form,[60]

$$a \approx L \ln V_0/kT, \tag{A1}$$

where

$$L = a_0(I_1 + I_3)/2^{\frac{1}{2}}I_H,$$

$$V_0 = 4I_H(Z_1Z_3)^{\frac{1}{2}}(I_1I_3/I_H^2),$$

a_0 is the Bohr radius, I_H is the ionization potential of hydrogen, I_1 and I_3 are the ionization potentials of the interacting atoms, and Z_1 and Z_3 are the charges of the
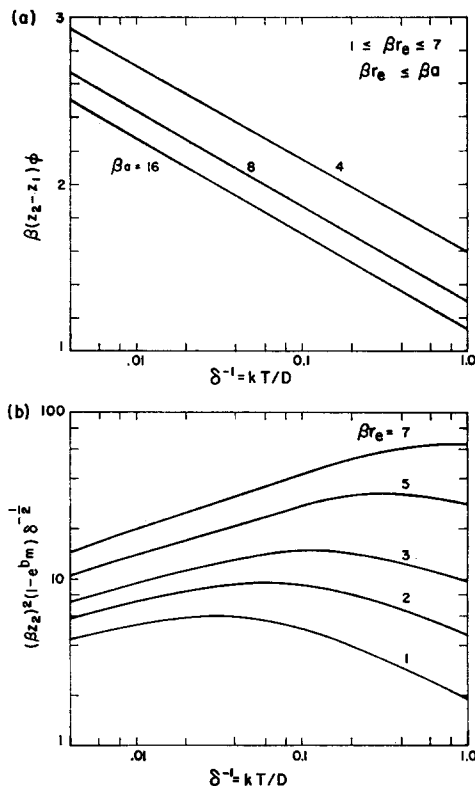

FIG. 4. Parametric curves for computing "barrier" rate constant (4.64).

interacting atoms. The Mason–Vanderslice potential gives a reasonable fit to the scattering cross sections of Amdur and co-workers and provides a simple method for estimating interactions which have not been measured. It does not include the van der Waals force, however, and cannot be used at low temperatures.