

Impulsive Collision Model for the Dissociation of Diatomic Molecules*†

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We investigate the dissociation rate of a dilute solution of diatomic molecules in an inert gas. The diatomic molecule is assumed to dissociate when its vibrational energy exceeds the dissociation energy E . A classical impulsive collision model is used for the interaction between the diatomic molecules and the solvent gas which is treated as a temperature bath at temperature T . The diatomic molecule is also simplified by treating it as one dimensional, thus neglecting the rotational degrees of freedom, and assuming that its translational degree of freedom is always in equilibrium when it is not neglected entirely. Still further simplification is achieved by considering only cases where the effect of the solvent gas may be represented by a transition rate between the vibrational energy states of the diatomic molecule, and the distribution function for vibrational energies $\epsilon \leq E$ is approximately given by the equilibrium distribution $F_0(\epsilon)$. We find *generally* (i.e., when the assumptions stated in the last sentence hold, but independent of our model) that when a diatomic molecule with vibrational energy E is very likely to lose (rather than gain) energy in a collision with a gas atom, the dissociation rate $k(E)$ is given by the expression $k(E) = \beta^{-1} [\tau(E)]^{-1} F_0(E)$, where $\tau(E)$ is the mean time between collisions for a molecule with vibrational energy E and β^{-1} is Boltzmann's constant times T . For the model considered in this paper, this will be the case when $E \gg (\gamma\beta)^{-1}$ where γ is the ratio of the mass of a gas atom to that of a diatomic molecule. The expression for $k(E)$ then assumes the simple form,

$$k(E) = \alpha A c \beta^{-1} e^{-\beta E} [\alpha(E)/Z(E)],$$

where A is the cross-sectional area for a collision, c is the concentration of gas atoms, $Z(E)$ is the vibrational partition function for the bound states, $\alpha(E)$ is the distance between the minimum and maximum value of the vibrational coordinate when the molecule is on the threshold of dissociation, and α is a constant of order unity. We also treat the case when $\gamma \ll 1$, which leads to a Fokker-Planck type equation for the distribution function from which $k(E)$ is found for $\beta E \gg 1$. A quasi-quantum-mechanical calculation for $k(E)$ is also presented and leads to the same results as the classical calculation.

I. INTRODUCTION

WE consider the problem of the dissociation of diatomic molecules immersed in a chemically inert gas, e.g., iodine molecules in argon gas. The physical situation may be visualized either by introducing a number of diatomic molecules (essentially in their ground state) into a gas at temperature T or starting with the system at some low temperature and suddenly raising the temperature of the inert gas, then observing the transfer of energy to the vibrational degree of freedom of the molecules which leads to their dissociation. We shall assume that the molecules behave as hard spheres connected by a spring which may break when the amplitude of vibration becomes sufficiently large. The atoms in the inert gas are also assumed to act like hard spheres, and the collisions between atoms and molecules are, therefore, impulsive, i.e., the duration of a collision is infinitesimally small compared to the time during which the position coordinates change significantly. This is the opposite of the adiabatic approxi-

mation, used by Landau and Teller,¹ where the duration of a collision is assumed long compared to a vibration period. This latter assumption leads to the conclusion that only small amounts of energy can be transferred during a collision. This conclusion also results from a perturbation expansion in the interaction, assumed weak, between the diatomic molecule and its surroundings. The impulsive collision model, on the other hand, permits a large transfer of momentum and, hence, energy during a collision. The actual energy transfer is determined by the momentum of the particles prior to a collision. We shall further assume that the distribution of gas atoms prior to collision is always Maxwellian at some temperature T . This permits us to write down an explicit equation for the time evolution of the distribution function $\rho(\mathbf{p}, \mathbf{q}, t)$ of the diatomic molecules in their phase space Γ , whose coordinates \mathbf{p} and \mathbf{q} , are the set of momentum and position variables of a diatomic molecule. The equation obeyed by $\rho(\mathbf{p}, \mathbf{q}, t)$ is an integro-differential equation which is a generalization of the Liouville equation for an ensemble of systems (the system here being a single diatomic molecule) interacting with surrounding heat reservoirs (the inert gas atoms are here considered the heat reservoir). On the basis of the assumptions outlined above the effect of the reservoirs on the evolution of $\rho(\mathbf{p}, \mathbf{q}, t)$ is completely

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‡ Part of this work was performed while the author was a visitor at Bell Telephone Laboratory, Murray Hill, New Jersey, and at Yeshiva University.

¹ L. Landau and E. Teller, *Physik. Z. Sowjetunion* **10**, 34 (1936).

characterized by a kernel $K(\mathbf{p}, \mathbf{q}; \mathbf{p}', \mathbf{q}')$. $K(\mathbf{p}, \mathbf{q}; \mathbf{p}', \mathbf{q}')$ $\times d\mathbf{p}'d\mathbf{q}'dt$ is the contingent probability that a molecule with coordinates \mathbf{p}', \mathbf{q}' will suffer a collision with a gas atom in the time interval dt , and as a consequence of this, will jump into the volume element $d\mathbf{p}d\mathbf{q}$ about the point \mathbf{p}, \mathbf{q} . Calling $H(\mathbf{p}, \mathbf{q})$ for Hamiltonian of the diatomic molecule, the equation for $\rho(\mathbf{p}, \mathbf{q}, t)$ has the form,²

$$\frac{\partial \rho}{\partial t} + (\rho, H) = \int [K(\mathbf{p}, \mathbf{q}; \mathbf{p}', \mathbf{q}')\rho(\mathbf{p}', \mathbf{q}', t) - K(\mathbf{p}', \mathbf{q}'; \mathbf{p}, \mathbf{q})\rho(\mathbf{p}, \mathbf{q}, t)] d\mathbf{p}'d\mathbf{q}', \quad (1.1)$$

where (ρ, H) is the Poisson bracket of ρ and H which represents the effect of the natural streaming (uninterrupted by collisions) in the phase space.

It is clear that the function $\rho(\mathbf{p}, \mathbf{q}, t)$ is sufficient to determine all the properties of the diatomic molecules (assumed independent). It is, unfortunately, also clear that even with the drastic simplifications of the nature of reservoir we have made, this function cannot be found in practice. However, when we are interested only in the dissociation rate, i.e., whether the two atoms making up the molecule are bound together or not, some drastic simplifications in the structure of the diatomic molecule, which make it a model of a dissociating molecule become reasonable, i.e., the model still contains the essential features of the process. The simplest procedure is to consider the vibrational degree of freedom separately and treat dissociation as the escape of particles from a potential well. This is the model treated by Kramers,³ Chandrasekhar,⁴ Montroll and Shuler,⁵ Buff⁶ and Careri.⁷ We shall consider this model first though we shall later generalize it to include also a translational degree of freedom, albeit in one dimension only.

The model molecule which we will consider consists thus of two pistons with some potential ϕ , possessing a minimum and a maximum between them. This molecule is embedded in a gas of atoms of mass m and concentration c , both outside and inside the pistons (this appears to represent best the three-dimensional situation). The cross-sectional area for hard-sphere collisions, on one dimension, between each piston and a gas atom is A . Neglecting further the translational degree of freedom, our system reduces to a single piston of cross-sectional area $2A$, effective mass M , moving in a potential $\phi(q)$ where q is now the relative position coordinate, measured from its equilibrium value. The relevant part of the molecular Hamiltonian H , and the

kernel K now have the form

$$H = (p^2/2M) + \phi(q), \quad (1.2)$$

$$K(p, q; p', q') = \frac{Ac}{m} \left(\frac{\beta}{8\pi m} \right)^{1/2} (1+\gamma)^2 |p-p'|$$

$$\times \exp \left\{ -\frac{\beta(1+\gamma)^2}{8m} \left[p - \frac{\gamma-1}{\gamma+1} p' \right]^2 \right\}$$

$$\times \delta(q-q'), \quad (1.3)$$

where $\gamma = m/M$, and the δ function appears because there is no change in position during the impulsive collision.⁸ We still have to choose the potential $\phi(q)$. The simplest choice, used by many authors, is that of a cutoff harmonic potential, having a maximum amplitude of vibration Q and a dissociation energy $E = \frac{1}{2}\kappa Q^2$. This potential is clearly wrong for large negative values of q (where it ought to become infinite) and, perhaps even more important, gives too steep a slope for $\phi(q)$ at $q=Q$. Despite these deficiencies, its use so greatly simplifies the problem that we shall use it for our explicit calculations in Sec. IV. Our general result Eqs. (3.6) and (3.12), is independent of the exact nature of $\phi(q)$ requiring only that it have a finite cutoff and some other qualitative features. This rules out the use of the Morse potential, which has no cutoff, without some modification.

The evolution of the distribution function $\rho(p, q, t)$ may now be looked at in terms of the unperturbed trajectories in the system's two-dimensional phase space (Fig. 1). The curve labeled E bounds the region $H(p, q) < E$, which we shall call $V(E)$, while the two vertical lines $q=Q_+$ and $q=Q_-$ define the region where the coordinate of the diatomic molecule lies whenever its energy is less than that necessary for dissociation. The trajectories in the region $V(E)$ are closed curves while those outside are open. Hence, in the absence of the solvent gas, a molecule initially inside the $V(E)$ will always remain there. Due to collisions with the gas particles, however, a molecule can jump from a point p', q' inside $V(E)$ to a point p, q' outside $V(E)$ and then dissociate. Since we are considering a very dilute concentration of diatomic molecules, we may neglect the possibility of recombination of the two parts of the diatomic molecule once they are apart, i.e. $q < Q_-$ or

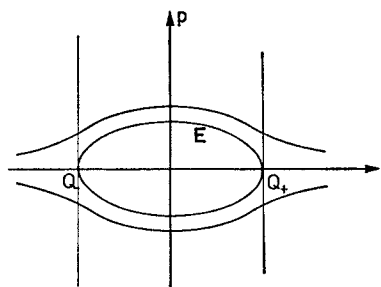


FIG. 1. The phase space of the vibrational degree of freedom of a diatomic molecule.

² P. G. Bergmann and J. L. Lebowitz, Phys. Rev. **99**, 578 (1955).
J. L. Lebowitz and P. G. Bergmann, Ann. Phys. (N. Y.) **1**, 1 (1957).

³ H. A. Kramers, Physica **7**, 284 (1940).

⁴ S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

⁵ E. Montroll and K. Shuler, in *Advances in Chemical Physics* (Interscience Publishers, Inc., New York, 1958), Vol. 1, p. 361.

⁶ F. P. Buff and D. J. Wilson, J. Chem. Phys. **32**, 677 (1960).

⁷ G. Careri, in *Advances in Chemical Physics* (Interscience Publishers, Inc., New York, 1958), Vol. 1, p. 119; J. Chem. Phys. **21**, 749 (1953).

$q > Q_+$. (This is particularly clear in the true three-dimensional situation to which we want our model to apply.) Furthermore, we shall also neglect the possibility that after the molecule has suffered a collision which took it out of the region $V(E)$, but before it has a chance to completely dissociate, i.e., leave the region $Q_- < q < Q_+$, it will suffer another collision which will bring it back into $V(E)$. This is certainly correct when the average time between collisions of the molecule with the gas is of the same order or larger than the period of vibration of the molecule, ω^{-1} and may, for other reasons, be correct in other cases (see Sec. V). We will, therefore, consider dissociation to occur whenever our system leaves the region $V(E)$ and neglect all transitions back into $V(E)$. The above assumption is formally equivalent to having an absorbing barrier at $H = E$, i.e., setting $\rho(p, q, t)$ equal to zero outside $V(E)$. This additional assumption is not essential, but is very convenient. It now permits us to go one step further in a consistent way and assume that even inside $V(E)$ ρ is a function only of the energy H . This will also permit us, as we shall see later, to go over easily to the corresponding quantum-mechanical treatment in terms of transition rates between energy levels.

The mathematical formulation of our problem before going over to the energy variable is then as follows: We want to find the concentration of diatomic molecules at time t , $C(t)$

$$C(t) = \int_{V(E)} \rho(p, q, t) dp dq, \quad (1.4)$$

given some initial distribution $\rho(p, q, 0)$ inside V . Since molecules can only leave but not enter $V(E)$, $C(t)$ will be a monotonically decreasing function of t approaching zero as $t \rightarrow \infty$. It is the rate at which $C(t)$ decreases that we are interested in here. This formulation of the dissociation problem is very similar to that of Montroll and Shuler⁵ but different from the formulation of Kramers³ and Chandrasekhar.⁴ The latter attach great importance to the backflow of particles from the region $q < Q_-$, $q > Q_+$. It is assumed by them in fact that there is a quasistationary state set up in which the net flow at Q is proportional to the concentration there. They are led to this formulation by considering the effect of the medium on the diatomic molecule to be similar to that exerted on a Brownian particle. This leads to the possibility of building up a concentration of molecules in the region $q < Q_-$, $q > Q_+$ which are ready for recombination. Considering, however, the scale of distances involved here and the fact that we are in reality dealing with a three-dimensional system, we believe their assumptions to be reasonable only for the case of very dense gases or liquids.

This difference in the formulation of the problem is responsible for the difference in the form of the dissociation rate constant k obtained by us when $\gamma = (m/M) \ll 1$ and that obtained by Kramers and Chandrasekhar. When $\gamma \ll 1$, the integrodifferential

equation (1.1), reduces to a Fokker-Planck type equation for ρ , having the same form as that used by Kramers. This equation yields, in our treatment,

$$k = 4Ac(8\gamma/\pi\beta M)^{1/2}\beta E e^{-\beta E} = \eta\beta E e^{-\beta E},$$

where η is the appropriate friction coefficient. This is in marked contrast to the result of Chandrasekhar [Eq. (507), Ref. 4] where, (taking note of the entirely different notation), k depends on the frequency ω and on the form of the potential in the region $q > Q_+$ and E does not appear in the pre-exponential factor at all.

II. REDUCTION OF PROBLEM TO ENERGY VARIABLE ONLY

Continuing now further with the development of our model, we introduce the kernel $K(\epsilon, \epsilon')$ which represents the probability density per unit time that a molecule with vibrational energy ϵ' , i.e., located on the surface $H(p', q') = \epsilon'$, corresponding to a microcanonical distribution with energy ϵ' , suffers a collision and jumps to the surface $H(p, q) = \epsilon$. $K(\epsilon, \epsilon')$ is determined by $K(p, q; p', q')$ through the relation

$$K(\epsilon, \epsilon') = [\Omega(\epsilon')]^{-1} \int K(p, q; p', q') \delta[H(p, q) - \epsilon] \times \delta[H(p', q') - \epsilon'] dp dq dp' dq'. \quad (2.1)$$

Here, $\Omega(\epsilon')$ is the "area" of the energy surface $H = \epsilon'$, which is given by the well-known expression

$$\Omega(\epsilon) = \frac{d}{d\epsilon} V(\epsilon) = \int \delta[H(p, q) - \epsilon] dp dq. \quad (2.2)$$

$\Omega(\epsilon)$ is finite for $\epsilon \leq E$ and for a simple harmonic potential is equal to $2\pi/\omega$. The kernel $K(\epsilon, \epsilon')$ derived from (1.3) satisfies the detailed balance condition

$$K(\epsilon, \epsilon') e^{-\beta\epsilon'} \Omega(\epsilon') = K(\epsilon', \epsilon) e^{-\beta\epsilon} \Omega(\epsilon). \quad (2.3)$$

The number of molecules whose vibrational energy is between ϵ and $\epsilon + d\epsilon$, $f(\epsilon) d\epsilon$, is given in terms of $\rho(p, q, t)$ by the relation

$$f(\epsilon, t) = \int \rho(p, q, t) \delta[H(p, q) - \epsilon] dp dq. \quad (2.4)$$

If $\rho(p, q, t)$ is a function of H only, then clearly

$$f(\epsilon, t) = [f(H(p, q), t)]_{H=\epsilon} \Omega(\epsilon). \quad (2.5)$$

Now, while the equation obeyed by $\rho(p, q, t)$ is Markoffian, i.e., the value of ρ at some time t' determines $\rho(t)$ for all later times $t, t > t'$, there is, in general no such equation for $f(\epsilon, t)$. Furthermore, even if ρ is initially a function of H only, it will generally not remain so. (This is also true in a quantum-mechanical system where ρ is replaced by the density matrix, or by the Wigner distribution function). The reason for this

is the correlation between the position of the system at a given point on an energy surface $\Omega(\epsilon)$ and the probability of a particular type of collision. When this correlation is not too important in its over-all effect, as will certainly be the case when the vibration period is smaller than the mean time between collisions, then we may neglect this correlation and write an equation for $f(\epsilon, t)$ directly. This will have the form

$$\frac{\partial f(\epsilon, t)}{\partial t} = \int [K(\epsilon, \epsilon')f(\epsilon', t) - K(\epsilon', \epsilon)f(\epsilon, t)]d\epsilon'. \quad (2.6)$$

The Liouville term, which does not cause transitions between different energies, does not appear here at all. Equation (2.6) is to be solved, in our formulation, subject to the boundary condition of an absorbing barrier at $\epsilon = E$. This may be incorporated explicitly in (2.6) by rewriting it in the form

$$\frac{\partial f(\epsilon, t)}{\partial t} = \int_0^E d\epsilon' [K(\epsilon, \epsilon')f(\epsilon', t) - K(\epsilon', \epsilon)f(\epsilon, t)] - f(\epsilon, t) \int_E^\infty K(\epsilon', \epsilon)d\epsilon', \quad \epsilon < E. \quad (2.7)$$

The first term here represents the effect of collisions in rearranging the distribution among the bound states while the second term represents the rate at which molecules with vibrational energy ϵ dissociate. The rate of change of the concentration of diatomic molecules is now given by

$$\frac{dC(t)}{dt} = \frac{d}{dt} \int_0^E f(\epsilon, t)d\epsilon = - \int_E^\infty d\epsilon \int_0^E K(\epsilon, \epsilon')f(\epsilon', t)d\epsilon'. \quad (2.8)$$

Introducing the normalized distribution $F(\epsilon, t)$

$$F(\epsilon, t) = C^{-1}(t)f(\epsilon, t); \quad \int_0^E F(\epsilon, t)d\epsilon = 1, \quad (2.9)$$

we have

$$k = -\frac{d \ln C}{dt} = \int_E^\infty d\epsilon \int_0^E K(\epsilon, \epsilon')F(\epsilon', t)d\epsilon'. \quad (2.10)$$

It will be meaningful to talk of a rate constant k only if (2.10) is approximately independent of the time. This would occur if $F(\epsilon, t)$ becomes approximately time-independent in a time short compared to k^{-1} from (2.10). The physical mechanism which might bring about this quasistationary value of F are the transitions between the bound-energy states represented by the first term on the right-hand side of (2.6). In the absence of the second term on the right-hand side of (2.6) $F(\epsilon, t)$ would tend towards the Maxwellian distribution $F_0(\epsilon)$:

$$F_0(\epsilon) = (e^{-\beta\epsilon}\Omega(\epsilon))/Z(E), \quad \epsilon < E, \quad (2.11)$$

where

$$Z(E) = \int_0^E e^{-\beta\epsilon}\Omega(\epsilon)d\epsilon. \quad (2.12)$$

This approach to $F_0(\epsilon)$ will be disturbed by the difference in the rates at which various bound levels are depleted to form the dissociated molecules, i.e., the ϵ dependence of the dissociation probability per unit time $\tau_d^{-1}(\epsilon, E)$

$$\tau_d^{-1}(\epsilon, E) = \int_E^\infty K(\epsilon', \epsilon)d\epsilon', \quad (2.13)$$

which might lead to a quasistationary F different from F_0 or preclude the existence of any such quasistationary F altogether. This problem has been investigated by many authors⁵ for various transition kernels, and it was found that when βE is sufficiently large, the use of $F_0(\epsilon)$ in (2.10) yields a very good value for k . This is not too surprising, as finding k corresponds to finding the lowest eigenvalue of the operator on the right-hand side of Eq. (2.7). Neglecting the last term of this operator we see that the smallest eigenvalue is zero, corresponding to the equilibrium distribution $F_0(\epsilon)$. When βE is large the lowest eigenvalue of the perturbed operator is extremely small, and one would then expect that the above determination of it, which is essentially a first-order perturbation calculation, would give a good result.

III. A GENERAL EXPRESSION FOR k WHEN $\beta E \gg 1$

We start from Eq. (2.10) with $F(\epsilon, t)$ replaced by $F_0(\epsilon)$,

$$k(E) = \int_E^\infty d\epsilon \int_0^E K(\epsilon, \epsilon')[e^{-\beta\epsilon'}/Z(E)]\Omega(\epsilon')d\epsilon'. \quad (3.1)$$

We now differentiate k with respect to E ,

$$\frac{dk}{dE} = - \int_0^E K(E, \epsilon')F_0(\epsilon')d\epsilon' + \int_E^\infty K(\epsilon', E)F_0(E)d\epsilon' - k \frac{d \ln Z(E)}{dE}. \quad (3.2)$$

Using the detailed balance property of $K(\epsilon, \epsilon')$, Eq. (2.3), we may rewrite (3.2) in the form

$$\begin{aligned} \frac{dk}{dE} &= -F_0(E) \left[\int_0^E K(\epsilon', E)d\epsilon' - \int_E^\infty K(\epsilon', E)d\epsilon' \right] \\ &\quad - k \frac{d \ln Z(E)}{dE}, \quad (3.3) \\ &= -F_0(E) [\tau^{-1}(E) - 2\tau_d^{-1}(E)] - k \frac{d \ln Z(E)}{dE}, \end{aligned}$$

where $\tau^{-1}(\epsilon)$ is the mean time between collisions for particles distributed uniformly over the energy surface $H = \epsilon$,

$$\tau^{-1}(\epsilon) = \int_0^\infty K(\epsilon', \epsilon) d\epsilon', \tag{3.4}$$

and $\tau_d^{-1}(\epsilon)$ has been defined in (2.11). The bracket on the right-hand side of (3.3) represents the difference for a system initially at E , between the probability per unit time that it will lose or gain energy in a collision with a gas particle.

We expect, in general, that for any hard collision model the first term in the bracket will give the largest

contribution to (3.3) when $\beta E \gg 1$ and γ is not too small. Assuming this to be the case, we have

$$\frac{dk}{dE} \sim -\frac{1}{\tau(E)} \frac{e^{-\beta E} \Omega(E)}{Z(E)}; \quad \beta E \gg 1, \quad \gamma \sim 0(1). \tag{3.5}$$

The term which varies most rapidly with E is presumably $e^{-\beta E}$, yielding

$$k \sim \Omega(E) e^{-\beta E} / \beta Z \tau(E). \tag{3.6}$$

We are now left with the task of computing $\tau^{-1}(E)$. This is most easily done by starting with $\tau^{-1}(p')$ and averaging it over the energy surface $\Omega(E)$. Now

$$\begin{aligned} \frac{1}{\tau(p')} &= \int_{-\infty}^\infty K(p, p') dp = \mathcal{C} \int_{-\infty}^\infty |p - p'| \exp\{-a(p + bp')^2\} dp \\ &= \mathcal{C} \left[\int_{-\infty}^\infty (p' - p) \exp\{-a(p + bp')^2\} dp + 2 \int_{p'}^\infty (p - p') \exp\{-a(p + bp')^2\} dp \right] \\ &= \mathcal{C} \left[(1+b)(\pi/a)^{1/2} p' + 2 \int_{p'}^\infty (p - p') \exp\{-a(p + bp')^2\} dp \right] \\ &= \mathcal{C} \left[(1+b)(\pi/a)^{1/2} |p'| + \frac{1}{a} \exp\{-a(1+b)^2 p'^2\} - 2(1+b) |p'| \int_{(1+b)|p'|}^\infty e^{-ay^2} dy \right], \end{aligned} \tag{3.7}$$

where

$$(1+b) = \frac{2}{1+\gamma}, \quad a = \frac{\beta}{8m} (1+\gamma)^2, \quad \mathcal{C} = \frac{Ac(1+\gamma)^2 \beta^{1/2}}{\pi^{1/2} (2\gamma M)^{3/2}}. \tag{3.8}$$

When $\beta E \gg \gamma^{-1}$ the first term will dominate over most of the surface $H = E$. Thus,

$$\frac{1}{\tau(p')} \propto |p'| \tag{3.9}$$

and

$$\begin{aligned} \frac{1}{\tau(E)} &= \frac{1}{\Omega(E)} \int \frac{1}{\tau(p')} \delta\left(\frac{p^2}{2M} + \Phi(q') - E\right) dp' dq' \\ &\approx \mathcal{C}(1+b) \left(\frac{\pi}{a}\right)^{1/2} \frac{2M}{\Omega(E)} \int |p'| \delta(p'^2 - 2M(E - \Phi(q'))) dp' dq' \\ &= \mathcal{C}(1+b) \left(\frac{\pi}{a}\right)^{1/2} \frac{2M}{\Omega(E)} \int \frac{p' \delta[p' - 2M(E - \Phi(q'))]}{[2M(E - \Phi(q'))]^{1/2}} dp' dq' \\ &= \mathcal{C}(1+b) \left(\frac{\pi}{a}\right)^{1/2} \frac{2M}{\Omega(E)} \int_{Q-}^{Q+} dq' = \mathcal{C}(1+b) \left(\frac{\pi}{a}\right)^{1/2} 2M \mathcal{Q} / \Omega(E), \end{aligned} \tag{3.10}$$

where \mathcal{Q} is the sum of the maximum displacements in the positive and negative directions. Putting in the constants we finally have

$$[1/\tau(E)] = 4Ac [\mathcal{Q}/\Omega(E)], \tag{3.11}$$

$$k = 4Ac \beta^{-1} e^{-\beta E} (\mathcal{Q}/Z), \quad \text{for } \beta E \gg 1, \quad \gamma = 0(1). \tag{3.12}$$

The term (\mathcal{Q}/Z) is the only one which depends on $\Phi(q)$. For the harmonic potential

$$\begin{aligned} \Phi(q) &= \frac{1}{2} M \omega^2 q^2, \quad |q| < Q \\ &= \frac{1}{2} M \omega^2 Q^2, \quad |q| \geq Q; \end{aligned} \tag{3.13}$$

hence

$$E = \frac{1}{2} M \omega^2 Q^2 = \frac{1}{2} M \omega^2 \left(\frac{\mathcal{Q}}{2}\right)^2,$$

or

$$\alpha = -\left(\frac{8E}{\omega M}\right)^{1/2}. \quad (3.14)$$

Also,

$$\Omega(E) = 2\pi/\omega, \quad Z(E) = (2\pi/\beta\omega)(1 - e^{-\beta E}).$$

Thus, for $\beta E \gg 1$,

$$\begin{aligned} \tau^{-1}(E) &= 4Ac(2E)^{1/2}/\pi\sqrt{M} \\ k(E) &= [4Ac(2E)^{1/2}/\pi\sqrt{M}]e^{-\beta E}. \end{aligned} \quad (3.15)$$

The rate constant is not affected very much if we chose $\Phi(q)$ to be an anharmonic potential which has a maximum value equal to E for $q = Q_+$. We have then

$$\begin{aligned} \Phi(q) &= \frac{1}{2}M\omega_0^2q^2[1 - \frac{2}{3}q/Q_+], \quad Q_- \leq q \leq Q_+ \\ &= \frac{1}{6}M\omega_0^2Q_+^2, \quad \text{otherwise;} \\ Q_- &= -\frac{1}{2}Q_+, \quad \alpha = |Q_-| + Q_+ = \frac{1}{\omega_0} \left(13.5 \frac{E}{M}\right)^{1/2}. \end{aligned} \quad (3.16)$$

$Z(E)$ is more difficult to evaluate now but should be very close to $2\pi/\beta\omega$ so that $k(E)$ will remain very close to that given in (3.15).

IV. EVALUATION OF k FOR $\gamma \approx 1$

We shall carry out here a more detailed calculation for the case of almost equal masses and a cutoff harmonic potential. This will lead again to Eq. (3.15) when $\beta E \gg 1$, thereby justifying, for this case at least, the assumption involved in going from Eq. (3.3) to Eq. (3.4).

To simplify the presentation we shall first discuss the case $\gamma = 1$, that is, equal masses for gas atoms and oscillator atoms. For this case we have [Eq. (1.3)]

$$\begin{aligned} K(p, q, p', q') &= \frac{Ac}{M} \left(\frac{2\beta}{\pi M}\right)^{1/2} |p - p'| \delta(q - q') \\ &\quad \times \exp\left(-\beta \frac{p^2}{2M}\right), \end{aligned} \quad (4.1)$$

where M is the common mass of the atoms.

To find $K(\epsilon, \epsilon')$ we consider first the function $K(\epsilon, p', q')d\epsilon$ which is the probability per unit time, that the system, initially at p', q' , will make a transition to an energy surface between ϵ and $\epsilon + d\epsilon$. Clearly,

$$K(\epsilon, p', q') = \int K(p, q; p', q') \delta[H(p, q) - \epsilon] dp dq. \quad (4.2)$$

Using (1.2) and (4.1), and carrying out the integration over q , we obtain

$$\begin{aligned} K(\epsilon, p', q') &= (Ac/m)(2\beta/\pi m)^{1/2} e^{-\beta \epsilon} e^{\beta \Phi(q')} \\ &\quad \times \int |p - p'| \delta[p^2/2m + \Phi(q') - \epsilon] dp. \end{aligned} \quad (4.3)$$

The argument of the delta function will vanish for $p = \pm [2m(\epsilon - \Phi(q'))]^{1/2}$. When $\epsilon > H(p', q')$, p' will lie between these two values of p , and (4.3) will yield

$$K(\epsilon, p', q') = 2Ac \left(\frac{2\beta}{\pi m}\right)^{1/2} e^{-\beta \epsilon} e^{\beta \Phi(q')} \quad (4.4)$$

for $\gamma = 1$ and $\epsilon > H(p', q')$. To obtain $K(\epsilon, \epsilon')$ we have to average $K(\epsilon, p', q')$ over the energy surface $H(p', q') = \epsilon'$,

$$\begin{aligned} K(\epsilon, \epsilon') &= [\Omega(\epsilon')]^{-1} \int K(\epsilon, p', q') \delta[\epsilon' - H(p', q')] dp' dq' \\ &= 2Ac \left(\frac{2\beta}{\pi m}\right)^{1/2} e^{-\beta \epsilon} \langle e^{\beta \Phi(q')} \rangle_{\epsilon'} \\ &= \frac{2\sqrt{2}Ac\sqrt{\beta}}{(\pi M)^{1/2}} e^{-\beta(\epsilon - \epsilon')} \langle e^{-\beta p'^2/2M} \rangle_{\epsilon'}. \end{aligned} \quad (4.5)$$

The evaluation of $\langle e^{\beta \Phi} \rangle$ can be carried out readily for the *harmonic potential* by going over to action angle variables,

$$\langle e^{\beta \Phi(q')} \rangle_{\epsilon'} = \frac{1}{2\pi} \int_0^{2\pi} e^{\beta \epsilon' \cos^2 \theta} d\theta \quad (4.6)$$

$$= 2I_0(\epsilon'/2) e^{\beta \epsilon'/2},$$

where I_0 is the hyperbolic Bessel function of order zero. That is, $I_0(z) = J_0(iz)$ where $J_0(z)$ is the ordinary Bessel function of order zero, and for large z we have asymptotically⁹ $I_0(z) = (2\pi z)^{-1/2} e^z$.

This leads finally to the result

$$\begin{aligned} K(\epsilon, \epsilon') &= \frac{4Ac(2\beta)^{1/2}}{(\pi M)^{1/2}} e^{-\beta(\epsilon - \epsilon')} \\ &\quad \times e^{-\beta \epsilon'/2} I_0(\beta \epsilon'/2), \quad \epsilon \geq \epsilon', \end{aligned} \quad (4.7)$$

and using detailed balance, Eq. (2.3),

$$K(\epsilon, \epsilon') = \frac{4Ac(2\beta)^{1/2}}{(\pi M)^{1/2}} e^{-\beta \epsilon'/2} I_0(\beta \epsilon'/2), \quad \epsilon \leq \epsilon'. \quad (4.8)$$

We see from Eq. (4.8) that the probability of a transition from ϵ' to ϵ , which increases the energy, $\epsilon > \epsilon'$, depends strongly on ϵ' . Thus, for $\beta \epsilon' \gg 1$, we have $[K(\epsilon, \epsilon')/K(\epsilon, \epsilon' + \delta)] = e^{-\beta \delta}$ for $\epsilon > \epsilon' + \delta$, $\delta > 0$. This might appear at first surprising since for equal masses the transition probability $K(p, p')$ goes essentially as $e^{-\beta p'^2/2M}$ which is independent of p' . The $e^{-\beta(\epsilon - \epsilon')}$ dependence of $K(\epsilon, \epsilon')$ for $\epsilon > \epsilon'$ is due to the fact that since the position does not change during a collision a system initially on the surface $H = \epsilon'$ can make transitions to only part of the surface $H = \epsilon$. The smaller ϵ' the higher

⁸ J. L. Lebowitz, Phys. Rev. **114**, 1192 (1959).

⁹ N. G. DeBruijn, *Asymptotic Methods in Analysis* (North-Holland Publishing Company, Amsterdam, 1958).

must the final kinetic energy be for a transition to ϵ . This does not apply to transitions which decrease the energy and there is no such factor there.

Substituting this value of $K(\epsilon, \epsilon')$ into Eq. (3.1) yields for the dissociation constant of a molecule with a cutoff oscillator potential and $\gamma=1$,

$$k(E) = \frac{4Ac(2\beta)^{1/2}e^{-\beta E}}{(\pi M)^{1/2}(1-e^{-\beta E})} \int_0^E e^{-\beta\epsilon'^{1/2}} I_0(\beta\epsilon'/2) d\epsilon' \quad (4.9)$$

$$= \frac{8Ac\sqrt{2}e^{-\beta E}\sqrt{E}}{(\pi^3 M)^{1/2}(1-e^{-\beta E})} \left[\int_0^{(\beta E)^{1/2}} \frac{(1-e^{-y^2})dy}{y^2[1-y^2(\beta E)^{-1}]^{1/2}} \right] \xrightarrow{\beta E \gg 1} \frac{4Ac(2E)^{1/2}e^{-\beta E}}{\pi M^{1/2}} [1+o(\beta E)^{-1}].$$

This agrees with Eq. (3.15) and thus confirms the analysis in Sec. III. It would be quite easy to compute higher order terms for the asymptotic form of $k(E)$ in Eq. (4.9). However, this form of $k(E)$, Eq. (3.1), is based on the assumption that the energy distribution $F(\epsilon)$ is, for $\epsilon < E$, adequately represented by $F_0(\epsilon)$ and this can be an adequate approximation only if $\beta E \gg 1$. Actually in order to get a good value for $k(E)$, we need the value of $F(\epsilon)$ for those energies ϵ , $\epsilon \leq E$, from which dissociation takes place. In our model this corresponds to a width β^{-1} . We expect $F_0(\epsilon)$ to be a good approximation for a given ϵ if the frequency of transitions between ϵ and other bound states is much greater than the frequency of transitions which lead to dissociation $\tau^{-1}(\epsilon) \gg \tau_d^{-1}(\epsilon)$. According to Eqs. (4.7) and (4.8) the ratio between these two type of transitions is of order βE for $\epsilon \lesssim E$. Hence, the replacement is consistent, if and only if $E\beta \gg 1$.

A similar analysis can be carried out for the case $\gamma \neq 1$. Unfortunately, however, the simplifications which occurred in the evaluation of (4.2) for $\gamma=1$ now no longer occur. Using the kernel (1.3) in (4.2) we find, for $\epsilon > H(p', q')$,

$$K(\epsilon, p', q') = \frac{Ac(1+\gamma)^2\sqrt{\beta}}{[2\pi\gamma^3 M]^{1/2}} e^{-\beta(\epsilon-\epsilon')} \sum \left\{ \frac{(\lambda \pm (2M)^{1/2} p')}{\lambda} \right.$$

$$\left. \times \exp \left[-\frac{\beta}{4\gamma} \left(\frac{(1+\gamma)p'}{(2M)^{1/2}} \pm (1-\gamma)\lambda \right)^2 \right] \right\}, \quad (4.10)$$

where $\lambda = [\epsilon - \Phi(q')]^{1/2}$, and the summation goes over the plus and minus signs. To obtain $K(\epsilon, \epsilon')$, (4.10) has to be averaged over the surface $H(p', q') = \epsilon'$. Considering again the case of a harmonic potential and going over to action angle variables we find

$$K(\epsilon, \epsilon') = \frac{Ac(1+\gamma)^2\sqrt{\beta}}{[2\pi\gamma^3 M]^{1/2}\pi} e^{-\beta(\epsilon-\epsilon')} \int_0^{2\pi} d\theta \left[\frac{(\epsilon - \epsilon' \sin^2\theta)^{1/2} - \sqrt{\epsilon' \cos\theta}}{(\epsilon - \epsilon' \sin^2\theta)^{1/2}} \right]$$

$$\times \exp \left\{ -\beta \frac{[(1-\gamma)(\epsilon - \epsilon' \sin^2\theta)^{1/2} - (1+\gamma)\sqrt{\epsilon' \cos\theta}]^2}{4\gamma} \right\}, \quad \epsilon \geq \epsilon'. \quad (4.11)$$

In order to find $k(E)$ from (3.1), when $\beta E \gg 1$ and γ is of 0(1), we need, as noted before, to know $K(\epsilon, \epsilon')$ for values of ϵ and ϵ' lying in the range, $E \leq \epsilon \leq E + \beta^{-1}$, $E - \beta^{-1} \leq \epsilon' \leq E$. It is, therefore, sufficient, when the above conditions on βE and γ are satisfied to evaluate the integral in (4.11) for $\beta\epsilon \gg 1$ and $[1 - \gamma/(1+\gamma)]^2 \epsilon < \epsilon' \leq \epsilon$. In this range (4.11) can be evaluated using Laplace's method,⁹ and we obtain, using also detailed balance,

$$K(\epsilon, \epsilon') = \begin{cases} \frac{2Ac(1+\gamma)}{\pi[2\gamma M]^{1/2}} \frac{e^{-\beta(\epsilon-\epsilon')}}{\left[\epsilon' - \left(\frac{1-\gamma}{1+\gamma} \right)^2 \epsilon \right]^{1/2}}; & \left(\frac{1-\gamma}{1+\gamma} \right)^2 \epsilon < \epsilon' \leq \epsilon \\ \frac{2Ac(1+\gamma)}{\pi[2\gamma M]^{1/2}} \frac{1}{\left[\epsilon - \left(\frac{1-\gamma}{1+\gamma} \right)^2 \epsilon' \right]^{1/2}}; & \epsilon' \geq \epsilon \geq \left(\frac{1-\gamma}{1+\gamma} \right)^2 \epsilon', \beta\epsilon \gg 1, \beta\epsilon' \gg 1. \end{cases} \quad (4.12)$$

and $K(\epsilon, \epsilon')$ vanishes approximately for other values of ϵ' when $\beta\epsilon \gg 1$. When (4.12) is used in (3.1) we again obtain (3.15).

V. THE FOKKER-PLANCK APPROXIMATION

We now discuss the case where the mass ratio of the gas particles to the diatomic molecule, γ , is so small that $\gamma\beta E$ is small compared to one even though we shall assume that βE is large compared to one. For this case the integrodifferential equation (1.1) may be reduced to a differential equation of the Fokker Planck type.^{8,10-12} Following Keilson and Storer¹¹ we expand the term on the right-hand side of the Liouville equation (1.1) in the following way:

$$\int [K(p, p')\rho(p', q, t) - K(p', p)\rho(p, q, t)]dp' = \sum \frac{1}{n!} \frac{d^n}{dp^n} [\alpha^{(n)}(p)\rho(p, q, t)], \quad (5.1)$$

where

$$\alpha^{(n)}(p) = \int K(p', p)(p - p')^n dp'. \quad (5.2)$$

In this way we write the integral operator as a differential operator of infinitely high order which we subsequently shall simplify by neglecting the higher terms.

With the kernel used here we have,⁸ setting $p - p' = z$

$$\begin{aligned} \alpha^{(n)}(p) &= \frac{2Ac\beta^{1/2}(1+\gamma)^2}{4(2\pi)^{1/2}(M\gamma)^{3/2}} \int_{-\infty}^{\infty} |z| z^n \exp\left\{-\beta \frac{[z + \gamma(z - 2p)]^2}{8M\gamma}\right\} dz \\ &= \frac{Ac\beta^{1/2}(1+\gamma)^2}{\pi^{1/2}(2M\gamma)^{3/2}} \int_{-\infty}^{\infty} |z| z^n \exp\left\{-\beta \frac{z^2(1+\gamma)^2}{8M\gamma}\right\} \left[1 + \frac{z\beta}{2M} + \dots\right] dz. \end{aligned} \quad (5.3)$$

Retaining only the lowest order terms in γ which contain the essential features of the problem we get

$$\alpha^{(1)} = 4Ac \left(\frac{8\gamma}{\beta\pi M}\right)^{1/2} p \quad (5.4)$$

$$\alpha^{(2)} = 8Ac \left(\frac{8\gamma}{\beta^3\pi M}\right)^{1/2} M. \quad (5.5)$$

The higher order terms vanish to this order⁸ so that the integral operator to this approximation becomes

$$4Ac \left(\frac{8\gamma}{\beta\pi M}\right)^{1/2} \left[\frac{\partial}{\partial p} \left(p + M\beta^{-1} \frac{\partial}{\partial p} \right) \right], \quad (5.6)$$

and the generalized Liouville equation reduces to the Fokker-Planck equation

$$\frac{\partial \rho}{\partial t} + \frac{p}{M} \frac{\partial \rho}{\partial q} - \frac{d\phi}{dq} \frac{\partial \rho}{\partial p} = \eta \left(p + M\beta^{-1} \frac{\partial}{\partial p} \right) \rho, \quad (5.7)$$

where ϕ is the molecular potential and the friction coefficient is

$$\eta = 4Ac \left(\frac{8\gamma}{\beta\pi M}\right)^{1/2}. \quad (5.8)$$

To find the rate constant for dissociation of the diatomic molecule we change to energy angle variables and assume as before that the density in phase space

depends only on the energy of the oscillator and on time, not on the angle variable.

The justification given before this assumption, namely that the time between collisions is larger than the period of vibration so that the phases are essentially randomly distributed is no longer valid. When γ is small the concentration of gas atoms must be very large (and hence, the time between collisions very small) in order for the gas to have any effect on the molecule. However, since the energy change in each collision is very small, the change in energy of the oscillator will be slow compared to its change in phase and thus averaging over the phase should still be approximately valid. This is similar to the justification for using energy variables rather than the distribution function (or the density matrix) in weak interaction theories of dissociation of diatomic molecules.^{5,13} We thus neglect here precisely the effect which is believed to be the rate determining step in the dissociation of polyatomic molecules, namely the getting in phase with respect to stretching of a bond.¹⁴

Assuming that after the transformation to energy angle variables ϵ, θ the density function F is only a function of ϵ and t we get

$$\frac{\partial F}{\partial t} = \eta \frac{\partial}{\partial \epsilon} \left[\epsilon \left(1 + \beta^{-1} \frac{\partial}{\partial \epsilon} \right) \right] F \quad (5.9)$$

as discussed previously.^{13,15} The solution to this equation

¹³ T. A. Bak and K. Andersen, Kgl. Danske Videnskab. Selskab, Mat. Phys. Medd. **33**, No. 7 (1961).

¹⁴ N. B. Slater, *Theory of Unimolecular Reactions* (Cornell University Press, Ithaca, New York, 1959).

¹⁵ T. A. Bak and I. W. Plesner, Acta Chem. Scand. **14**, 1310 (1960).

¹⁰ J. E. Moyal, J. Roy. Stat. Soc. (London) **B11**, 150 (1949).

¹¹ J. Keilson and J. E. Storer, Quart. Appl. Math. **10**, 243 (1952).

¹² A. Siegel, J. Math. Phys. **1**, 378 (1960).

which is zero for $\epsilon = E$ can be expressed in terms of the confluent hypergeometric function

$$F = e^{-\beta\epsilon} \sum C_n e^{-\eta a_n t} {}_1F_1(-a_n, 1, \beta\epsilon), \quad (5.10)$$

where $C_n (n=0, 1, 2, \dots)$ are determined by the initial conditions and $a_n (n=0, 1, 2, \dots)$ are the roots of the equation ${}_1F_1(-a, 1, \beta E) = 0$.

If $\beta E \gg 1$ the roots of this transcendental equation become approximately $0, 1, 2, \dots$ and, therefore, the rate constant as defined above [Eq. (2.10)] becomes independent of time (except for $t \lesssim \eta^{-1}$) and equal to ηa_0 . The problem of determining the rate constant then reduces to determining the smallest positive root a_0 of the equation ${}_1F_1(-a, 1, \beta E) = 0$ or, alternatively, to find the smallest eigenvalue of the operator

$$-\frac{\partial}{\partial \epsilon} \left(1 + \beta^{-1} \frac{\partial}{\partial \epsilon} \right) \quad (5.11)$$

with the boundary condition that the eigenfunction vanishes at $\epsilon = E$. A number of methods have previously been used in solving this problem.¹³

The formal method which lends itself most easily to this case is the variational method which gives an approximation to the smallest eigenvalue as

$$a_0 = \frac{\int_0^{\beta E} \left(\frac{d}{d\epsilon} \psi(\epsilon) + \psi(\epsilon) \right)^2 \epsilon e^{\beta\epsilon} d\epsilon}{\int_0^{\beta E} [\psi(\epsilon)]^2 e^{\beta\epsilon} d\epsilon}, \quad (5.12)$$

where $\psi(\epsilon)$ is an approximation to the eigenfunction corresponding to the smallest eigenvalue. In this case it would not be a good approximation to use for ψ the equilibrium distribution $F_0(\epsilon)$ since the dissociation here takes place from a very small region near $\epsilon = E$, where the correct quasistationary distribution differs significantly from F_0 by going to zero for $\epsilon \rightarrow E$. However, as long as one is only interested in large values of E , ψ may with sufficient accuracy be taken as $e^{-\beta\epsilon} - e^{-\beta E}$ which gives $a_0 \approx \beta E e^{-\beta E}$. The method itself is, of course, only of minor interest in connection with the harmonic oscillator, since in that case the eigenfunctions are known, and the eigenvalue a_0 can be found from the series expansion of the confluent hypergeometric function. The method can, however, equally well be used to find the rate constant for escape from an arbitrary potential.¹³

With this result for a_0 , we now have the expression for the rate constant quoted above:

$$k = 4Ac \left(\frac{8\gamma}{\beta\pi M} \right)^{1/2} \beta E e^{-\beta E}, \quad (5.13)$$

whose most important features are that the pre-exponential factor is proportional to the energy, to the

square root of the mass of the gas atoms, and inversely proportional to the square root of the temperature.

VI. CENTER OF MASS NOT FIXED

So far we have neglected the translational and rotational motion of the molecule altogether. We shall now relax the restriction on translational motion and consider a diatomic molecule constrained to move on a straight line. We shall, however, still assume that the translational motion of the center of gravity is in thermal equilibrium *at all times*.

Let P_1, Q_1 and P_2, Q_2 be the coordinates of the two atoms in the molecule, P, Q the coordinates of the center of gravity and p, q the relative coordinates. Since the interaction with the gas atoms is impulsive we have that during a collision between one end of a molecule and a gas atom the other end of the molecule does not change its momentum or its position. Introducing

$$P_1 = \frac{1}{2}P - p,$$

$$P_2 = \frac{1}{2}P + p,$$

and integrating over the center-of-mass coordinates in Eq. (1.1) we obtain an equation containing only the relative coordinates with the kernel

$$K(p, q, p', q') = \frac{2Ac(1+\gamma)^2 \sqrt{\beta}}{M^{3/2} \pi^{1/2} \gamma (\gamma+2)} |p-p'| \times \exp \left\{ -\frac{\beta[p' - (1+\gamma)p]^2}{(\gamma+2)M} \right\} \delta(q-q'), \quad (6.1)$$

which allows us to calculate k , using the methods outlined above.

For the case $\gamma \approx 1$ we get, using the method of Sec. IV,

$$k = \frac{8Ac(1+\gamma)}{\pi M^{1/2} (\gamma+2)^{1/2}} E^{1/2} e^{-\beta E} \{ 1 + O[(\beta E)^{-1}] \}, \quad (6.2)$$

while for the case $\gamma \ll 1$, where the Fokker-Planck equation is valid, we obtain the same equation as before except that η now has only half of its previous value.

Whereas, the fixed center rate constant for $\gamma \approx 1$ [Eq. (3.15)] was independent of m (or γ), we have here a slight γ dependence.

The method which we have used here for the interaction of vibration and translation could also be used for the interaction of rotation and vibration which would occur in the three-dimensional problem.

VII. AN APPROXIMATE QUANTUM-MECHANICAL CALCULATION

As mentioned above an exact quantum-mechanical calculation seems presently to be impossible unless one wants to do it numerically as done by Shuler and

Zwanzig.¹⁶ As an alternative to the full quantum-mechanical treatment we shall now consider the quantum correction to the classical case which arises from dividing phase space into cells. We consider only the case $\gamma=1$ and fixed center of gravity of the oscillator for which $K(\epsilon, \epsilon')$ is given by Eqs. (4.7), (4.8). From this we want to calculate $K_{nn'}$, the probability of transition from quantum state n' to quantum state n . Since

the energy of the quantum state n is $E_n = (n + \frac{1}{2})\hbar\omega$ we define the quantum state n as the part of phase space for which the energy of the oscillator lies between $n\hbar\omega$ and $(n+1)\hbar\omega$.

To obtain $K_{nn'}$ we shall, therefore, integrate $K(\epsilon, \epsilon')$ over the final energies in the range $n\hbar\omega \leq \epsilon \leq (n+1)\hbar\omega$ and 'average' it over the initial energies, $n'\hbar\omega < \epsilon' < (n'+1)\hbar\omega$. Thus,

$$K_{n,n'} = \left[\int_{-\hbar\omega/2}^{\hbar\omega/2} dx \int_{-\hbar\omega/2}^{\hbar\omega/2} dz K(E_n + x, E_{n'} + z) e^{-\beta z} \right] / \left[\int_{-\hbar\omega/2}^{\hbar\omega/2} e^{-\beta z} dz \right]. \quad (7.1)$$

The use of the Boltzmann factor in averaging over the initial states is necessary in order that $K_{nn'}$ have the property of detailed balance in equilibrium:

$$K_{nn'} e^{-\beta E_{n'}} = K_{n'n} e^{-\beta E_n}.$$

Using (4.7) in (7.1) yields, for $\gamma=1$,

$$K_{n,n'} = 4Ac \left(\frac{2\beta}{\pi M} \right)^{1/2} \exp \left[-\beta \left(E_n - \frac{E_j}{2} \right) \right] \int_{-\hbar\omega/2}^{\hbar\omega/2} I_0 \left(\beta \frac{E_j}{2} + \frac{\beta z}{2} \right) e^{-\beta z/2} dz \quad [j = \min(n, n')]. \quad (7.2)$$

We note here that our $K_{nn'}$ has the property

$$K_{n+j, n'} / K_{n, n'} = e^{-\beta j \hbar \omega}; \quad n > n', \quad n+j > n'. \quad (7.3)$$

Thus, when $\beta \hbar \omega$ is not too large compared to unity there will be a reasonably large transition rate to levels for which $n - n' > 1$. The transition rate to levels $n < n'$ will be almost independent of n for $\beta E_{n'} \gg 1$. This is in contrast to the weak-interaction model⁶ where only transitions to neighboring levels are permitted.

Eq. (7.3) may be compared with the work of Schuler and Zwanzig¹⁶ who carried out numerical computations for the transition probabilities $K_{n,n'}$ for $0 \leq n, n' \leq 3$, $\beta \hbar \omega = 2$ and $\gamma = \frac{1}{2}$. Since (7.3) is only valid for $\gamma=1$, this makes a direct test of our quantum model impossible and might account for some of the discrepancy, which is relatively small, between our results and theirs. They find, for example, (Table I, Ref. 16), $[K_{1,0}/K_{2,0}] \simeq 9$, $[K_{2,0}/K_{3,0}] \simeq 8$, $[K_{2,1}/K_{3,1}] = 11$ while (7.3) predicts that all these ratios be equal to $e^2 \simeq 7.4$. We did not use their results for $K_{n,n}$ in the comparison for it is here where we would expect the crudeness of our quantum model to show up most strongly. This should, however, not have too great an effect on our calculation of the dissociation rate which we are now going to compute.

Let x_n be the population of the n th level of the oscillator and N the largest stable level. A particle which reaches the $(N+1)$ th vibrational level is thus immediately 'absorbed,' that is, the molecule dissociates and, as above, we neglect the possibility of particles returning from the states $n \geq N+1$. The populations of

the levels satisfy the equations

$$\frac{dx_n}{dt} = \sum_{n' \neq n}^N K_{nn'} x_{n'} - x_n \sum_{n' \neq n}^{\infty} K_{n'n} = \sum_{n'=0}^N A_{nn'} x_{n'} \quad (n=0,1,2,3, \dots, N). \quad (7.4)$$

If there were no dissociation ($N = \infty$) Eq. (7.4) would have a stationary solution, namely, the equilibrium distribution. When the states above N are absorbing, we no longer consider an infinite matrix, since we are not interested in \dot{x}_n for $n > N$. We have now

$$\dot{\mathbf{x}} = \mathbf{A}\mathbf{x} = (\mathbf{A}_0 + \delta\mathbf{A})\mathbf{x}$$

where \mathbf{x} is the vector (x_0, x_1, \dots, x_N) , \mathbf{A}_0 is an $N \times N$ matrix which represents the transitions between the bound levels and $\delta\mathbf{A}$ is an $(N \times N)$, negative, diagonal matrix which represents the transitions to the dissociated states. \mathbf{A}_0 by itself has a lowest eigenvalue of zero corresponding to the equilibrium distribution, $F_0(n) = Z^{-1}(N) e^{-\beta E_n}$.

Let $\lambda_n (n=0,1, \dots, N)$ be the eigenvalues of \mathbf{A} . The solution of the differential equation (7.4) is then

$$x_n = \sum C_{nn'} e^{-\lambda_n t}, \quad (7.5)$$

where $C_{nn'}$ can be determined from the initial conditions. Following the same argument as before, we see that the rate constant for dissociation, to an approximation which is better the larger N is, will be given by the negative value of the numerically smallest eigenvalue λ_0 of \mathbf{A} . We shall compute λ_0 by the use of perturbation theory.

The use of perturbation theory to find λ_0 is equivalent to assuming an equilibrium distribution among the

¹⁶ K. E. Shuler and R. Zwanzig, *J. Chem. Phys.* **33**, 1778 (1960). See also F. H. Mies and K. E. Shuler, *ibid.* **37**, 117 (1962).

bound states. As already discussed in Sec. IV this is a good approximation for our model when $\beta E_N = \beta(N+1)\hbar\omega \gg 1$. In this situation transition from a state n' , even when n' is close to or equal to N , will be much more frequent to nondissociating than to dissociating levels. This is not the case for the weak interaction theory. The numerically smallest eigenvalue of \mathbf{A} which we want to find is the zero eigenvalue of \mathbf{A}° which has been perturbed by $\delta\mathbf{A}$. We, therefore, symmetrize \mathbf{A}° by the transformation $y_n = x_n \exp(\frac{1}{2}\beta E_n)$, $B_{nm} = A^\circ_{nm} \exp[\beta\hbar\omega(n-m)/2]$, whereby we obtain

$$\frac{d}{dt}\mathbf{y} = (\mathbf{B} + \delta\mathbf{A})\mathbf{y}. \quad (7.6)$$

Let ψ_0 be the normalized eigenvector of \mathbf{B} corresponding to eigenvalue zero. The numerically smallest eigenvalue of $\mathbf{B} + \delta\mathbf{A}$ is then $\psi_0 \cdot (\delta\mathbf{A})\psi_0$. We have then

$$\psi_0 = \left\{ \frac{1}{\sqrt{Z'_N}}, \frac{e^{-\beta\hbar\omega/2}}{\sqrt{Z'_N}}, \frac{e^{-\beta\hbar\omega}}{\sqrt{Z'_N}}, \dots, \frac{e^{-N\beta\hbar\omega/2}}{\sqrt{Z'_N}} \right\}, \quad (7.7)$$

where $Z'_N e^{-\beta\hbar\omega/2}$ is the partition function for the bound states, Z_N , that is $|\psi_0|^2$ is the equilibrium distribution for the bound states. Substituting ψ_0 in the expression for the perturbed eigenvalue we obtain again *precisely* Eq. (4.9) for $k(E)$ with $E = (N+1)\hbar\omega$.

Since the above perturbational calculation leads to the same result as Eq. (3.1) it is at least very probable that the latter procedure will, in general, have the same property, as the ordinary perturbational procedure, namely, that the eigenvalue approximation is better than the eigenfunction approximation.

VIII. DISCUSSION AND CONCLUSION

The main result of this work is combined in the equation

$$k = \frac{1}{\beta Z(E)\tau(E)} \Omega(E) e^{-\beta E}, \quad (8.1)$$

and the explicit calculations of $\tau(E)$ for various models all leading essentially to the result [Eq. (3.11)]

$$1/\tau(E) = 4AcQ/\Omega(E).$$

Although this paper deals only with the one-dimensional case, the above equation for k should be valid in the limit $\beta E \gg 1$ also for a three-dimensional system. In that case, the calculation of $\tau(E)$ will be somewhat more complicated.

The derivation of the equation above is based on the integral equation for F , which in our present formalism implies hard-sphere interaction, and on the assumption $\beta E \gg 1$ which is necessary for the evaluation of certain

integrals. It is clear that the approximation of a hard-sphere interaction will be good when the time of vibration of the diatomic molecule is large compared to the time of interaction, i.e., the time it takes a gas atom at thermal energies to travel over a distance equal to the range of the interaction.

For a real diatomic molecule the vibrational frequency decreases with increasing vibrational energy and for such a molecule the hard-sphere approximation will be good for transitions between high-energy levels. In addition the approximation will always be good for transitions caused by very fast molecules, i.e., when the mass ratio γ is small or at very high (translational) temperatures of the gas. For the model considered in detail here the vibrational frequency (or the spacing of the energy levels) is independent of the energy and a high-vibrational energy of the molecule, therefore, by itself does not assure us the validity of the approximation. Since our main result [Eq. (8.1)], however, is independent of the exact form of the intramolecular potential this result presumably remains correct in the above mentioned cases. It should be remembered however, that multiple collisions in the sense of Widom¹⁷ have been neglected throughout but we believe this to cause only a small error in the three-dimensional case to which our calculations eventually should apply.

In order to compare the results with experiments¹⁸ we consider the dissociation of iodine in argon. For this, the measured rate constant in the range 298–418°K is

$$k = 2.40 \times 10^{15} \exp(-\beta E) - 5.30 \times 10^{15} \times \exp(-\beta E) \text{ ml mole}^{-1} \text{ sec}^{-1}$$

with $E = 35\,500$ cal/mole.¹⁷ Substituting numbers in Eq. (6.2) and setting $A = (\pi/4)\sigma^2$ with σ measured in Å, we get $k = 1.13 \times 10^{13} \sigma^2 \exp(-\beta E)$. This shows that with a reasonable choice of σ , such that $\sigma^2 \approx 25 \text{ Å}^2$, the theoretical value is too small by a factor of about 12.

If we consider the dissociation of iodine in helium the experimental value of k at 298°K is $4.42 \times 10^{15} \times \exp(-\beta E)$ and the theoretical result, using Eq. (5.13), again is too low by a factor of about 12. At 1400°K the experimental rate constant is $1.76 \times 10^{14} \exp(-\beta E)$ and here the theoretical result is low only by a factor of less than 2.

The theory presented here, therefore, clearly does not solve completely the problem of the very large values of the dissociation rate constants of diatomic molecules, but we believe it is a significant improvement both over the simple collisions theory and over the weak-interaction stepwise-activation theories.

¹⁷ B. Widom, J. Chem. Phys. 28, 918 (1958).

¹⁸ For a review of experimental results, see A. F. Trotman Dickenson, *Gas Kinetics* (Butterworths Scientific Publications, Ltd., London, 1955).