DISSOCIATION OF DIATOMIC MOLECULES

Dissociation of Diatomic Molecules *

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A diatomic molecule is considered as two hard spheres connected by a spring. It is imbedded in a gas of hard-sphere atoms, which is assumed to be in thermal equilibrium at all times. Only a one-dimensional model is considered, and the possibility of multiple collisions during an encounter is neglected. The molecule is assumed to dissociate immediately whenever its vibrational energy exceeds E. The density in the phase space of the diatomic molecule is described by the Liouville equation for the isolated molecule with an added collision integral for collisions with the gas atoms. Since the gas is assumed in equilibrium this integral equation is linear. The rate constant for dissociations is found directly from the integral equation and (for small mass of the gas atoms) after its reduction to a Fokker-Planck equation.

We consider the dissociation of a symmetrical diatomic molecule in a chemically inert gas of monatomic particles. The gas is assumed to be in thermal equilibrium at all times. As an illustration one may think of a dilute solution of iodine molecules in an inert gas. The molecule is assumed to be two hard spheres connected by a spring and the gas atoms are assumed to be mass-points. The problem will be discussed classically and quantum-mechanically, using Bohr-Sommerfeld quantization. In order to simplify the calculations we shall treat only the one-dimensional case, so that the molecule would more correctly be described as two pistons connected by a spring. The criterion for reaction is taken to be that the vibrational energy of the molecule reaches a certain value E, which is assumed to be identical with the spectroscopic dissociation energy.

The reason for choosing this model is that the weak interaction theories, which have been the main centre of interest recently [1-4] generally give rate-constants which are much lower than the experimental values. The hard-core potential we have chosen here is certainly not realistic, but it will probably reveal the more important features of a strong interaction theory.

Although the present theory by the choice of interaction potential is a strong interaction theory, we can, by letting the concentration c of gas atoms go to infinity and the mass of the gas atoms go to zero (so that $c\sqrt{m}$ is finite), obtain a Fokker-Planck equation for the motion of the diatomic molecule in phase-space. In this way the present theory makes contact with weak interaction theories.

CLASSICAL THEORY

Let M be the mass of the atoms in the molecule, m the mass of the gas atoms and $\rho(p,q,t)$ the density in oscillator phase-space. Let us furthermore in the beginning assume that the centre of gravity of the diatomic molecule is fixed in space so that we consider the motion of one piston of mass M, cross-sectional area $2A$ and co-ordinates in phase-space p,q. The motion takes place in a harmonic potential (for

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energies smaller than E) and under the influence of bombardment by particles of mass m coming from a gas at equilibrium.

For the density in phase space we then have

$$\partial \rho / \partial t + (\rho, H) = \int K(p,q,p',q') \rho(p',q',t) \mathrm{d}p' \mathrm{d}q' - \rho(p,q,t) \int \int K(p',q',p,q) \mathrm{d}p' \mathrm{d}q' \qquad (1)$$

as derived by Bergmann and Lebowitz.[5]   Here (ρ,H) is the Poisson-bracket and the kernel $K(p,q,p',q')$ is

$$K(p,p',q,q') = \frac{2Acm(M+m)^2 \sqrt{\beta}}{\sqrt{(2\pi m)(2mM)^2}} |p-p'| \delta(q-q') \exp \left\{ -\frac{\beta[(1+\gamma)p - (1-\gamma)p']^2}{8m} \right\}, \qquad (2)$$

where $\gamma = m/M$ and $\beta = 1/kT$. Since the colliding particles are hard spheres, the co-ordinates of the particles do not change during an encounter and the kernel therefore contains $\delta(q-q')$.

In the derivation of this equation, multiple collisions in the sense of Widom[6] have been neglected. Since most cases amenable to an experimental investigation correspond to $\gamma < 1$, for which multiple collisions are of minor importance, this is presumably a reasonable approximation.

If, in the above equation, we change to energy-angle variables and assume the density in oscillator phase-space to be angle-independent, we get

$$\frac{\partial}{\partial t} \rho(\varepsilon,t) = \int K(\varepsilon,\varepsilon') \rho(\varepsilon',t) \mathrm{d}\varepsilon' - \frac{1}{\tau(\varepsilon)} \rho(\varepsilon,t), \qquad (3)$$

where ε is the vibrational energy of the oscillator and $\tau(\varepsilon) = [\int K(\varepsilon',\varepsilon) \mathrm{d}\varepsilon']^{-1}$ is the relaxation time for change of energy of the oscillator. The kernel $K(\varepsilon,\varepsilon')$ is related to $K(p,q,p',q')$ by

$$K(\varepsilon,\varepsilon') = \frac{\int K(p,q,p',q') \delta[H(p,q) - \varepsilon] \delta[H(p',q') - \varepsilon'] \mathrm{d}p \mathrm{d}q \mathrm{d}p' \mathrm{d}q'}{\mathrm{d}V(\varepsilon')/\mathrm{d}\varepsilon'}, \qquad (4)$$

where $V(\varepsilon)$ is the volume of phase space for which the energy of the oscillator is less than ε.

The rate constant for escape is now determined by summing $\rho(\varepsilon')K(\varepsilon,\varepsilon')$ over all initial energies $\varepsilon' < E$ and all final energies $\varepsilon > E$. This leak of particles out from the potential well will of course change ρ so that it is not the equilibrium distribution, but if the well is sufficiently deep we can, to a first approximation for ρ, use the equilibrium distribution $Z(E)^{-1} \exp(-\beta \varepsilon')$, where $Z(E)$ is the partition function for the bound states. This is essentially a perturbational approach, and the resulting rate constant will therefore approximate the true value of the rate constant better than the equilibrium distribution approximates the correct distribution. This argument leads to the following expression for the rate constant,

$$k = \int_E^\infty \mathrm{d}\varepsilon \int_0^E \frac{\exp(-\beta\varepsilon')}{Z(E)} K(\varepsilon,\varepsilon') \frac{\mathrm{d}V(\varepsilon')}{\mathrm{d}\varepsilon'} \mathrm{d}\varepsilon', \qquad (5)$$

and we shall see later in connection with the quantum case that the value of the rate constant obtained from this expression is identical with the one obtained by a more orthodox perturbation method.

The expression for k can be thought of as merely stating the rather obvious fact that the particles which escape from the potential minimum will not all jump from the bottom of the well. Rather there is a distribution of particles on the possible energy levels in the well, and from all these levels there is a possibility of leaving the

well in one jump.   Seen from this point of view the expression seems almost trivial, but one must remember that, without an explicit calculation of $K(\varepsilon,\varepsilon')$, it is still without any practical use.

It is convenient to rewrite the expression for k in the following manner,

$$\frac{dk}{dE} = -\int_0^E \frac{\exp(-\beta\varepsilon')}{Z(E)} K(E,\varepsilon') \frac{dV}{d\varepsilon'} d\varepsilon' + \int_E^\infty \frac{\exp(-\beta E)}{Z(E)} K(\varepsilon,E) \frac{dV}{dE} d\varepsilon - k\frac{d\ln Z}{dE},$$

since it is clear that the last two terms are negligible compared to the first.   Also in the first integral, we can extend the range of integration to ∞, since the interval $E < \varepsilon' < \infty$ contributes negligibly.   We therefore have

$$\frac{dk}{dE} = -\int_0^\infty \frac{\exp(-\beta\varepsilon')}{Z(E)} K(E,\varepsilon') \frac{dV}{d\varepsilon'} d\varepsilon',$$

and, using detailed balance in the form,

$$K(E,\varepsilon') \exp(-\beta\varepsilon')\left(\frac{dV}{d\varepsilon}\right)_{\varepsilon=\varepsilon'} = K(\varepsilon',E) \exp(-\beta E)\left(\frac{dV}{d\varepsilon}\right)_{\varepsilon=E},$$

we obtain

$$\frac{dk}{dE} = -\frac{\exp(-\beta E)}{Z(E)}\left(\frac{dV}{d\varepsilon}\right)_{\varepsilon=E}\int_0^\infty K(\varepsilon,E)d\varepsilon$$

$$= \frac{1}{Z(E)\tau(E)}\left(\frac{dV}{d\varepsilon}\right)_{\varepsilon=E} \exp(-\beta E).$$

The intuitive meaning of this is particularly striking, since it states that as the activation energy E is increased the rate of dissociation diminishes, because the flow of particles from the surface in phase-space where dissociation takes place back to the potential minimum is increased.

From this expression for the derivative of k we get

$$k = \frac{1}{\beta Z(E)\tau(E)}\left(\frac{dV}{d\varepsilon}\right)_{\varepsilon=E} \exp(-\beta E)\{1+0[(\beta E)^{-1}]\}, \tag{6}$$

which is our final expression for the rate constant.

To simplify the presentation, we shall only discuss in details the calculation of $K(\varepsilon,\varepsilon')$ for equal masses.   For this case, we have

$$K(p,q,p',q') = \frac{2Ac\sqrt{\beta}}{M\sqrt{\pi M}}|p-p'|\,\delta(q-q')\exp\left(-\beta\frac{p^2}{2M}\right), \tag{7}$$

where M is the common mass of the atoms.   To get the conditional probability that the oscillator goes from energy ε' to ε in the time dt we use eqn. (4).   The integration is most conveniently carried out after a change to energy-angle variables, since the integrations over the energies are immediate because of two of the δ-functions.   We are left with

$$K(\varepsilon,\varepsilon') = \frac{2Ac\sqrt{\beta}}{M\sqrt{\pi M}2\pi\omega}\int_0^{2\pi} d\theta \int_0^{2\pi} d\theta'\,|\sqrt{\varepsilon}\cos\theta - \sqrt{\varepsilon'}\cos\theta'|\,\exp(-\beta\varepsilon\cos^2\theta)\times$$

$$\partial\left(\sqrt{\frac{2\varepsilon}{\kappa}}\sin\theta - \sqrt{\frac{2\varepsilon'}{\kappa}}\sin\theta'\right), \tag{8}$$

where $\omega = \sqrt{\kappa/M}$ is the frequency of the oscillator and κ the spring constant.

The integration over θ is immediate when the δ-function is used giving, for $\varepsilon > \varepsilon'$,

$$K(\varepsilon,\varepsilon') = \frac{2Ac\sqrt{\beta}\exp(-\beta\varepsilon)}{M\sqrt{\pi M\pi\omega}}\int_0^{2\pi}\left|\sqrt{\varepsilon-\varepsilon'}\sin^2\theta - \sqrt{\varepsilon'}\cos\theta\right|\exp(\beta\varepsilon'\sin^2\theta')\times$$
$$\left[\frac{2\varepsilon}{\kappa}\left(1-\frac{\varepsilon'}{\varepsilon}\sin^2\theta'\right)\right]^{-\frac{1}{4}}d\theta'. \qquad (9)$$

Assuming $\beta\varepsilon' \gg 1$, this integral can be evaluated using Laplace's method,[7] i.e., expanding $\beta\varepsilon'\sin^2\theta'$ in the exponential function in powers around its maximum value and retaining only terms up to the second power.

In the rest of this integrand θ is replaced by the value for which the exponential function is largest, and that part thus reduces to a constant. Finally, the limits of integration are extended from $-\infty$ to ∞, since the integrand vanishes rapidly outside its maximum value. It is seen that in this case there are two values of θ, for which the exponential function has a maximum, namely $\theta = \pi/2$ and $\theta = 3\pi/2$, and that they contribute equally to the integral.

In this way we obtain

$$K(\varepsilon,\varepsilon') = \frac{2\sqrt{2}Ac}{\sqrt{M}\pi\sqrt{\varepsilon'}}\exp\left[-\beta(\varepsilon-\varepsilon')\right]; \quad \varepsilon \geqq \varepsilon', \qquad (10)$$

and using detailed balance we then have

$$K(\varepsilon,\varepsilon') = \frac{2\sqrt{2}Ac}{\sqrt{M}\pi\sqrt{\varepsilon}}; \qquad\qquad \varepsilon \geqq \varepsilon'. \qquad (11)$$

In both cases we have assumed that $\beta\varepsilon'$ is large compared to one, but since we want to use these transition probabilities to calculate the rate of transitions leading to chemical reactions, which in most cases will stem from transitions from fairly high energy levels, this is not a severe limitation.

Using these expressions for $K(\varepsilon,\varepsilon')$ we obtain

$$\frac{1}{\tau(E)} = \int_0^\infty K(\varepsilon,E)d\varepsilon = \frac{2\sqrt{2}Ac}{\sqrt{M}\pi}\left[\int_0^E\frac{1}{\sqrt{\varepsilon}}d\varepsilon + \frac{1}{\sqrt{E}}\int_E^\infty\exp(-\beta\varepsilon)d\varepsilon\right]$$
$$= \frac{2\sqrt{2}Ac}{\sqrt{M}\pi}\left[2\sqrt{E} + \frac{1}{\beta\sqrt{E}}\right],$$

where, to the approximation we use here, the last term in the bracket can be neglected. Since for a harmonic oscillator $Z(E) \approx Z(\infty) = 2\pi/\omega\beta$ and $V(\varepsilon) = 2\pi\varepsilon/\omega$, we finally obtain

$$k = \frac{4\sqrt{2}Ac}{\pi\sqrt{M}}\sqrt{E}\exp(-\beta E). \qquad (12)$$

When these calculations are repeated for $\gamma \neq 1$, one obtains precisely the same result for the rate-constant although the intermediate results for $K(\varepsilon,\varepsilon')$ differ somewhat from the results given above. The only interesting feature is that one finds for $\varepsilon > \varepsilon'$ that $K(\varepsilon,\varepsilon')$ is only significantly different from zero in the range,

$$\left(\frac{1-\gamma}{1+\gamma}\right)^2\varepsilon < \varepsilon' \leqq \varepsilon. \qquad (13)$$

This shows clearly that as $\gamma \to 0$, the energy range from which transitions to ε is possible becomes exceedingly narrow. We shall return to this point in connection with the Fokker-Planck equation.

So far, we have assumed that the centre of gravity of the molecule is fixed so that the molecule acts as a piston which has twice the area of a single piston, and which is anchored to a fixed point. To investigate the behaviour of a diatomic molecule constrained to move on a straight line through the atomic centres we introduce two collision kernels, one for each end of the molecule. We then express that during an impulsive collision between one end of the molecule and a gas atom the other end does not change momentum nor co-ordinate. Furthermore we assume that the translational motion of the centre of gravity is in thermal equilibrium at all times.

Let P_1, Q_1 and P_2, Q_2 be the co-ordinates of the two atoms in the molecule, P, Q the co-ordinates of the centre of gravity and p, q the relative co-ordinates. We then have

$$P_1 = \tfrac{1}{2}P - p,$$
$$P_2 = \tfrac{1}{2}P + p,$$

and

$$K(p,q,p',q') = \int K(P_1,Q_1,P_1',Q_1')\delta(P_2-P_2')\delta(Q_2-Q_2')\frac{\exp(-\beta P'^2/4M)}{\sqrt{4\pi M\beta^{-1}}}dPdP'dQdQ' +$$

$$\int K(P_2,Q_2,P_2',Q_2')\delta(P_1-P_1')\delta(Q_1-Q_1')\frac{\exp(-\beta P'^2/4M)}{\sqrt{4\pi M\beta^{-1}}}dPdP'dQdQ',$$

where $K(P_1', Q_1, P_1', Q_1')$ is the kernel for atom no. 1 and $K(P_2,Q_2,P_2',Q_2')$ is the kernel for atom no. 2, both given by eqn. (2). The integrals involved are all elementary and we obtain

$$K(p,q,p',q') = \frac{2Ac(1+\gamma)^2\sqrt{\beta}}{M^{\frac{3}{2}}\sqrt{\pi}\gamma(\gamma+2)}|p-p'|\delta(q-q')\exp\left\{-\frac{\beta[p'-(1+\gamma)p]^2}{(\gamma+2)M}\right\}. \quad (14)$$

Using this kernel we can determine $K(\varepsilon,\varepsilon')$ for this case and from that the rate constant, using the methods outlined above. We obtain

$$k = \frac{8Ac(1+\gamma)}{\pi\sqrt{M}\sqrt{\gamma+2}}\sqrt{E}\exp(-\beta E); \quad (15)$$

whereas the fixed centre rate constant was independent of m (or γ), we here have a slight γ-dependence. It is interesting to note that as $\gamma \to 0$ the two rate constants become identical, which is what one would expect, since in that case the translation of the centre of gravity becomes unimportant.

QUANTUM-MECHANICAL THEORY

An exact quantum mechanical theory of chemical dissociation seems, at present, to be impossible. 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 centre of gravity of the oscillator for which the kernel is given by eqn. (7). From this we want to calculate $K_{nn'}$, the probability of transition from quantum state n' to quantum state n. It is convenient to introduce a quantity $K(n,p',q')$ which gives the probability of transition from the classical state p',q' (with energy less than $(n+\frac{1}{2})\hbar\omega$) to the quantum state n. Since the energy of the quantum state n is $(n+\frac{1}{2})\hbar\omega$, 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 $(n+1)\hbar\omega$. Furthermore, the value of q is unchanged during a

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change in state since the collision is impulsive. For each value of q' and p' the oscillator can therefore jump down to a p-range,

$$-\sqrt{2M(n+1)\hbar\omega - M^2\omega^2 q'^2} < p < -\sqrt{2Mn\hbar\omega - M^2\omega^2 q'^2},$$

or up to a p-range,

$$\sqrt{2Mn\hbar\omega - M^2\omega^2 q'^2} < p < \sqrt{2M(n+1)\hbar\omega - M^2\omega^2 q'^2}.$$

The probability of transition to the quantum state n is therefore, provided the energy of the initial state is less than $(n+\frac{1}{2})\hbar\omega$,

$$K(n,p',q') = \frac{2Ac\sqrt{\beta}}{M\sqrt{2\pi M}} \int_{-\sqrt{2M(n+1)\hbar\omega - M^2\omega^2 q^2}}^{-\sqrt{2Mn\hbar\omega - M^2\omega^2 q^2}} (p'-p)\exp(-\beta p^2/2M)\mathrm{d}p +$$

$$\int_{\sqrt{2Mn\hbar\omega - M^2\omega^2 q^2}}^{\sqrt{2M(n+1)\hbar\omega - M^2\omega^2 q^2}} (p-p')\exp(-\beta p^2/2M)\mathrm{d}p$$

$$= \frac{4cA}{\sqrt{2\pi M\beta}} \exp\left(-\frac{\beta M}{2}\omega^2 q^2\right) \exp(-\beta n\hbar\omega)[1-\exp(-\beta\hbar\omega)].$$

To get $K_{nn'}$ we now average this over the values of p and q' which correspond to the energy surface $\varepsilon' = (n'+\frac{1}{2})\hbar\omega$, that is,

$$K_{nn'} = \frac{\int K(n,p',q')\delta[(n'+\frac{1}{2})\hbar\omega - (p'^2/2M) - \frac{1}{2}M\omega^2 q'^2]\mathrm{d}p'\mathrm{d}q'}{[\mathrm{d}V(\varepsilon')/\mathrm{d}\varepsilon']_{\varepsilon'=(n'+\frac{1}{2})\hbar\omega}}.$$

As before, the integral is most conveniently carried out in energy-angle variables and we obtain

$$K_{nn'} = \frac{4Ac}{\sqrt{2\pi M\beta}}[1-\exp(-\beta\hbar\omega)]\exp(-\beta n\hbar\omega)\exp\left(\frac{\beta n'\hbar\omega}{2}\right)I_0\left(\frac{\beta n'\hbar\omega}{2}\right),$$

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

From the value of $K_{nn'}$ for $n > n'$ we can get the transition probability for all values of n and n' by using detailed balance and we therefore have

$$K_{nn'} = \frac{4Ac}{\sqrt{2\pi M\beta}}[1-\exp(-\beta\hbar\omega)]\exp(-\beta n\hbar\omega)\exp\left(\frac{\beta v\hbar\omega}{2}\right)I_0\left(\frac{\beta v\hbar\omega}{2}\right), \qquad (16)$$

$$[v = \min(n,n')].$$

As a check on the correctness of this we note that assuming $\beta\hbar\omega \ll 1$ and $v \gg 1$ and using the asymptotic expression for I_0 we obtain the classical transition probability derived above.

Let x_n be the population of the nth 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 $n > N+1$. The populations of the levels satisfy the equations

$$\frac{\mathrm{d}x_n}{\mathrm{d}t} = \sum_{n'=n}^{N} K_{nn'}x_{n'} - x_n\sum_{n'=n}^{\infty} K_{n'n} = \sum_{n'=0}^{N} A_{nn'}x_{n'}, \qquad (17)$$

$$(n = 0, 1, 2, 3 \ldots N).$$

Following the method used by Montroll and Schuler,[1] we can now approximate the rate constant for dissociation by the numerical value of the numerically smallest eigenvalue of the matrix $A_{nn'}$. For $N \to \infty$, the numerically smallest eigenvalue is zero, and for finite N we can obtain the eigenvalue by conventional perturbation technique starting from the equilibrium solution, which corresponds to a zero eigenvalue. In this way we obtain

$$k = \frac{4\sqrt{2}Ac}{\pi\sqrt{M\beta\hbar\omega}}\sqrt{N\hbar\omega}[1 - \exp(-\beta\hbar\omega)] \exp[-\beta(N+1)\hbar\omega], \tag{18}$$

which is the quantum-mechanical expression for the rate constant. If $\beta\hbar\omega \ll 1$ we can expand the first bracket to get $1 - \exp(-\beta\hbar\omega)] \sim \beta\hbar\omega$ and the expression then to its classical value. The sole effect of the discrete levels of the oscillator is thus to cut down the rate with a factor $[1 - \exp[\omega\hbar\beta]/\beta\hbar\omega$ and the physical reason for this is that the oscillator now cannot split up an energy change $\hbar\omega$ on two or more jumps.

Since the above perturbational calculation in the classical limit leads to the same result as the closely related eqn. (5), it is at least very probable that the latter procedure will have the same property as the ordinary perturbational procedure, namely, that the eigenvalue approximation is better than the eigenfunction approximation.

THE FOKKER-PLANCK EQUATION

As has been shown by Keilson and Storer,[8] an integral equation of the type used above may be transformed into a differential equation of infinitely high order. We have

$$\int [K(p,q,p',q',t)\rho(p',q',t) - K(p',q',p,q,)\rho(p,q,t)]dp'dq = \sum_{n=1}^{\infty} \frac{1}{n!}\frac{d^n}{dp^n}[\mathscr{A}^{(n)}(p)\rho(p,q,t)], \tag{19}$$

where

$$\mathscr{A}^{(n)}(p) = \int K(p',q',p,q)(p-p')^n dp'dq'.$$

With the kernel used here, we have, retaining only terms up to $\sqrt{\gamma}$,

$$\mathscr{A}^{(1)} = 4Ac\sqrt{\frac{8\gamma}{\beta\pi M}}p,$$

$$\mathscr{A}^{(2)} = 8Ac\sqrt{\frac{8\gamma}{\beta^3\pi M}}M,$$

so that the integral operator to this approximation becomes

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

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

$$\frac{\partial\rho}{\partial t} + \frac{p}{M}\frac{\partial\rho}{\partial q} - \frac{dV}{dq}\frac{\partial\rho}{\partial p} = \eta\frac{\partial}{\partial p}\left(p + M\beta^{-1}\frac{\partial}{\partial p}\right)\rho, \tag{20}$$

where V is the molecular potential and the friction coefficient η is $4Ac\sqrt{8\gamma/\beta\pi M}$.

The coefficients $\mathscr{A}^{(n)}$ $(n > 2)$ contain only γ in higher powers than $\frac{1}{2}$ and as long as $\gamma \ll 1$, they can therefore presumably be neglected. It is seen, however, that the expansion is not simply an expansion in powers of $\gamma^{\frac{1}{2}}$. In order for the friction

coefficient to be finite, one must assume that as $\gamma \to 0$, $c \to \infty$, so that $c \sqrt{\gamma}$ stays finite. Only then does the integral operator change into a second-order differential operator.

It has been shown by Keilson and Storer, for a somewhat simplified kernel, that in spite of the different response of the two types of equations to an initial δ-distribution for small times, the two solutions will be almost identical for large times. Since the escape of a particle from a potential minimum is a slow process in the molecular time-scale, one might therefore expect that one will get the same rate constant from the Fokker-Planck equation as the one found above. This, however, is by no means the case. Writing the Fokker-Planck equation in energy-angle variables and assuming that the density in phase-space is independent of the angle, we get

$$\frac{\partial \rho}{\partial t} = \eta \frac{\partial}{\partial \varepsilon} \varepsilon \left(1 + \beta^{-1} \frac{\partial}{\partial \varepsilon}\right) \rho,$$

for which the solution which vanishes at $\varepsilon = E$ is[9]

$$\rho = \exp(-\beta \varepsilon) \sum_{n=0}^{\infty} C_n \exp(-\eta a_n t) {}_1F_1(-a_n, 1, \beta \varepsilon).$$

Here a_n are the roots of the equation ${}_1F_1(-a_n, 1, \beta E) = 0$, ${}_1F_1$ is the confluent hypergeometric function and the coefficients C_n are determined by the initial conditions. The rate constant is therefore approximately ηa_0 which by various methods discussed previously can be determined to be, in the limit $\beta E \gg 1$,

$$k_0 = \eta a_0 = 4Ac \sqrt{\frac{8\gamma}{\pi \beta M}} \beta E \exp(-\beta E). \tag{21}$$

It is seen that the energy dependence of the pre-exponential factor is quite different from that found before and since the previous expression was independent of γ, this is a peculiar result.

We believe these differences to be due to the very special limiting process used in obtaining the Fokker-Planck equation. Clearly, not both expressions can be correct, say for I_2 in He, but it is quite difficult to argue in favour of one of the results, rather than the other. It is perhaps significant that when terms proportional to γ are included in eqn. (20) and treated as a perturbation one gets

$$k = k_0[1 + \gamma(\beta E)^2/8] \tag{22}$$

which for instance for I_2 in He at 300°K gives an increase in the rate constant by about a factor of 12. This is quite a large perturbation and naturally leads to a certain scepticism about the validity of this whole approach.

CONCLUSION

The main purpose of this paper has been to show how a particular kind of strong interaction can be taken into account in dissociation reactions. The theory can, in principle, be extended to any kind of strong interactions by using a linearized Boltzmann equation rather than eqn. (1). The method which we have used to eliminate the translational motion of the molecule can also be used to eliminate the rotational motion when a three-dimensional problem is treated. In both cases, however, one encounters considerable mathematical difficulties.

Although the present work therefore has a preliminary character it is interesting to compare the conclusions with the experimental results. For I_2 in He, we have the following experimental values [10]: at 298°K, $k = 4.42 \times 10^{15} \exp(-E/RT) \text{ sec}^{-1}$,

and at 1400°K, $k = 1.76 \times 10^{14} \exp(-E/RT) \sec^{-1}$. The concentration c is measured in molecules/ml and E equals 35,500 cal/mole. Using eqn. (15) and setting $A = \pi\sigma^2$, we calculate from the rate constant $\sigma = 10.8$ Å at 298°K and $\sigma = 6.8$ Å at 1400°K. These σ-values are somewhat larger than the sum of the hard-core radii of I and He and the rate constant calculated from eqn. (15) will therefore be too low. The change in the calculated σ with temperature furthermore shows that the temperature dependence of eqn. (15) is incorrect. If instead, we use eqn. (22), we get too low σ-values, namely, 1.3 Å and 1.2 Å but here the temperature dependence comes out right. In view of the fact that the model is one-dimensional, the agreement must be considered largely fortuitous.

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