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DISSOCIATION OF DIATOMIC MOLECULES CONSIDERED AS DIFFUSION IN PHASE SPACE

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Synopsis

Dissociation of diatomic molecules is considered as the escape of a classical particle from a potential minimum due to its Brownian motion. The criterion for reaction is taken to be annihilation of the particle at a certain energy. For this model the Kramers equation is set up and solved exactly for potentials of the form $V = C|r|^n$, and the rate constant for escape from the potential minimum is found. It is also shown how the rate constant may be obtained from a variational principle, and as an example of this method the rate of escape from a Morse potential is found. The results obtained agree very well with machine calculations. Finally it is attempted to justify the Kramers equation in the limit of weak interaction by deriving it directly from the Liouville equation. It is shown that the equation obtained deviates significantly from the Kramers equation, except for the case of a harmonic oscillator molecule. It is remarkable, however, that rate constants obtained in this way for the rate of escape of a particle from very deep potentials of the above mentioned simple form are almost identical with those derived from the theory of Kramers.

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Introduction

In recent years there has been a renewed interest in stepwise activation theories of chemical reactions[1–5] resembling the Brownian motion theory originally proposed by KRAMERS[6]. In such a theory the reacting molecule is considered as an effective mass point which performs a Brownian motion in an external potential due to the coupling to a thermostat. When the particle attains a sufficiently high energy a chemical reaction may occur, which in these theories is pictured as the crossing of a certain surface in phase-space, or simply as an annihilation of the particle as it reaches a certain energy.

Due to the Brownian motion of the particle in phase space the probability density function for the particle will satisfy a diffusion equation when the problem is treated classically, or a discrete analogue of a diffusion equation when it is treated quantum mechanically. It is generally assumed that the diffusion equation derived by Kramers using the semiphenomenological theory of Brownian motion is correct. So far it has only been possible, however, to compare it with more exact calculations in the case of a particle moving in a harmonic oscillator potential, since only in this case has it been possible to set up the equations. In the harmonic oscillator case, and with the assumption that the density in phase space does not depend on the angle variable of the particle, there is complete agreement between the classical equation of KRAMERS[6] and the equation derived by BAK, GOCHE and HENIN[7] for the case of the Brownian motion of an oscillator weakly coupled to a crystal lattice. Furthermore, for this case the quantum mechanical theory of MONTROLL and SHULER[1] also reduces to the Kramers equation in the limit $\hbar \to 0$.

In the case of a harmonic oscillator potential it is also comparatively simple to solve the diffusion equation, at least when the reaction is considered as an annihilation of particles. As is usual for such calculations, the rate constants obtained for the dissociation of diatomic molecules are far too small. One of the reasons for this is undoubtedly the use of the harmonic potentials, since one would expect that an anharmonic potential would speed up the dissociation reaction. Although the neglect of anharmonicity in the potential is by no means the only reason for the discrepancy between theory and experiments, we shall here be concerned solely with this difficulty and disregard such questions as the relative importance of hard core collisions and weak interaction collisions, and the even more elusive question of whether it is permissible to use intermolecular potentials, derived by using the Born-Oppenheimer approximation, under the conditions which prevail in a molecular collision.

Throughout this paper we shall therefore assume that the reacting molecule, which we for simplicity shall think of as a diatomic molecule, is in weak interaction with a thermostat. The thermostat which is assumed to be in equilibrium may be a gas or a crystal (phonon gas). The criterion for reaction is that the molecule reach a certain energy, i. e., the reaction is pictured as an annihilation at a certain energy level.

For this model we derive the Kramers diffusion equation in phase space (or rather energy-time space) and solve it exactly for oscillator potentials $V = C\,|r|^n$. For arbitrary intermolecular potentials the equation can be solved approximately be a variational method. As an example of the use of this method, we find the rate constant for escape from a Morse potential.

Finally we attempt to justify the Kramers equation for the above model by deriving it directly from the Liouville equation, using the asymptotic time integration developed by BROUT and PRIGOGINE[12].

Due to mathematical difficulties we limit ourselves in this case to considering the oscillator potentials $V = C\,|r|$, $V = \frac{1}{2}\gamma r^2$ and the square-well potential, $V = 0$ for $|r| < l/2$, $V = \infty$ for $|r| > l/2$. These potentials have the common feature that when r is expressed in terms of the action-angle variables, J and r can be factorized, i. e. $r = r_0(J)\,\theta(\alpha)$.

In order to be able to compare the coefficients C, γ and l for these potentials one must make a convention about the different values of r at which dissociation occurs. We shall make the assumption that the value of r at which dissociation occurs is the same for the three potentials. We therefore have

$$C^2 = \frac{1}{2} D\gamma \qquad \text{and} \qquad l^2 = 2\,D/\gamma$$

where D is the activation energy.

The most remarkable feature of the exact theory is that it gives practically the same results for the rate of escape of a particle from a potential as does the theory of Kramers, in spite of the fact that the two equations for the time behaviour of the density in phase space are completely different. We cannot, however, agree with the statement made by MAZUR[15] that Prigogine's theory confirms the phenomenological theory of Kramers. The agreement which one obtains with respect to rate constants indicates, however, that as long as only weak interactions are considered, the conceptually much simpler theory of Kramers which has later been elaborated by BRINKMAN[16] may be useful when considering the influence of anharmonicities, or when investigating the validity of annihilation as criterion for reaction.

Both the theory of Kramers and the more exact treatment based on Prigogine's integration of the Liouville equation show that for simple potentials one gets the result that the rate constant is

$$k \propto \frac{1}{\omega(\beta D)} \beta D\, e^{-\beta D}$$

which is precisely the result one would expect from a correspondence argument assuming the result

$$k = \beta D\, e^{-\beta D}$$

to be valid for the harmonic oscillator where the energy levels are equally spaced. Both theories therefore show that anharmonicities which decrease the frequency of vibration increase the rate of dissociation, in qualitative accord with the experimental findings. The aim of the present paper is, however, not to compare theory and experiments, but solely to study how the problem of anharmonic molecular potentials can be treated within the framework of a weak interaction theory.

Kramers' equation

We shall start by giving a derivation of the Kramers equation for diffusion in phase space for the case of small viscosity, i. e., weak interaction between the particle, the Brownian motion of which we consider, and the thermostat. The derivation takes its starting point in the Fokker-Planck-equation for the phase-density function $\Phi = \Phi(q, p, t)$, defined in the phase-space for the particle. In the case of a particle exposed to a force derived from an external field of force $V(q)$ in addition to the stochastically varying force due to the surrounding medium, the equation has the following form[6, 8]

$$\frac{\partial \Phi}{\partial t} = \eta \frac{\partial}{\partial p}\left(\Phi p + m\beta^{-1}\frac{\partial \Phi}{\partial p}\right) - \frac{p}{m}\frac{\partial \Phi}{\partial q} + \frac{dV}{dq}\frac{\partial \Phi}{\partial p}. \tag{1}$$

For our purpose it turns out to be practical to change the variables specifying the state of motion of the particle from (q, p) to action-angle variables $J = \frac{1}{2\pi}\int p\,dq$, which depends only on the energy, and α defined by $d\alpha = \omega\,dt$ where $\omega = \frac{2\pi}{T} = \frac{dE}{dJ}$. For the simple case where $dq = \frac{p}{m}dt$ we have therefore

$$J = \int_0^T \frac{p^2}{m}\,dt = \frac{2\pi}{\omega}\int_0^{2\pi}\frac{p^2}{m}\,d\alpha. \tag{2}$$

We now consider the case where the coupling-coefficient η can be taken to be so small that the particle will run through the region in phase space between the surfaces with constant energy E and $E + dE$ several times (α increasing each time by 2π) before it leaves this region and changes its energy. Expressed in another way, we suppose the particle density to be equally distributed over the region between E and $E + dE$, that is $\Phi = \Phi(J)$ or $\left(\frac{\partial\Phi}{\partial\alpha}\right)_J = 0$. Substituting

$$\frac{\partial}{\partial p} = \frac{\partial J}{\partial p}\frac{\partial}{\partial J} = \frac{p}{\omega m}\frac{\partial}{\partial J} \quad \text{and} \quad \frac{\partial}{\partial q} = \frac{\partial J}{\partial q}\frac{\partial}{\partial J} = \frac{1}{\omega}\frac{dV}{dq}\frac{\partial}{\partial J}$$

into eq. (1) and introducing the reduced energies $x = \beta E$ and reduced action variables $j = \beta J$, eq. (1) is transformed into

$$\frac{\partial\Phi}{\partial t} = \eta\left[\Phi + \beta\left(\frac{p^2}{\omega m} + \frac{1}{\omega} + \frac{p^2}{\omega m}\frac{d}{dj}\left(\frac{1}{\omega}\right)\right)\frac{\partial\Phi}{\partial j} + \beta\frac{p^2}{\omega^2 m}\frac{\partial^2\Phi}{\partial j^2}\right].$$

Then integrating (averaging) over α from 0 to 2π using eq. (2), the following partial differential equation is obtained

$$\frac{\partial\Phi}{\partial t} = \eta\frac{\partial}{\partial j}\left(\Phi j + \frac{j}{\omega}\frac{\partial\Phi}{\partial j}\right) = \eta\omega\frac{\partial}{\partial x}j\left(1 + \frac{\partial}{\partial x}\right)\Phi \tag{3}$$

where in the last equation Φ is considered as a function of the reduced energy x and t instead of j and t. Introducing the reduced time $\tau = \eta t$ we get

$$\frac{\partial\Phi}{\partial\tau} = \omega\frac{\partial}{\partial x}j\left(1 + \frac{\partial}{\partial x}\right)\Phi$$

and separating the variables by setting

$$\Phi(x, \tau) = \Psi(x)\,\Theta(\tau)$$

we obtain

$$\frac{1}{\Theta}\frac{d\Theta}{d\tau} = \frac{1}{\Psi}\,\omega\,\frac{d}{dx}\,j\left(1+\frac{d}{dx}\right)\Psi = -k.$$

As Φ has to approach a stationary function for $\tau \rightarrow \infty$, the solution for Θ must be $\Theta \propto e^{-k\tau}$ with k positive and real. For Ψ we therefore obtain the differential equation

$$\omega\,\frac{d}{dx}\,j\left(1+\frac{d}{dx}\right)\Psi + k\Psi = 0.$$

Because we are primarily interested in the deviation from the Maxwell-Boltzmann distribution, we set $\Psi(x) = y(x)\,e^{-x}$, and obtain for y

$$\frac{d}{dx}\left(j\,e^{-x}\frac{dy}{dx}\right) + k\,e^{-x}\left(\frac{y}{\omega}\right) = 0 \tag{4}$$

or

$$j\omega\,\frac{d^2y}{dx^2} + (1-j\omega)\frac{dy}{dx} + ky = 0. \tag{5}$$

Furthermore, for the special potentials, which can be expressed by $V(q) = C\,|\,q^n\,|$ $\left(C \text{ being a constant, } 0 \leqq q \leqq \left(\frac{E}{C}\right)^{1/n}\right)$ as for example the square-well or the harmonic potential, $j\omega$ will be proportional to x as a consequence of the virial theorem. This can be shown simplest by introducing $p = \pm\sqrt{2\,m\,(E-V)}$ in the expression defining J when the potential is symmetrical about $q = 0$.

$$J = \frac{1}{2\,\pi}\oint p\,dq = 4\,\frac{1}{2\,\pi}\sqrt{2\,m}\int_0^{(E/C)^{1/n}}\sqrt{E - C\,q^n}\,dq.$$

When $q = z\left(\frac{E}{C}\right)^{1/n}$ is substituted we get

$$J = \frac{4}{2\,\pi}\sqrt{2\,m}\,C^{-1/n}\,E^{(1/2+1/n)}\int_0^1\sqrt{1-z^n}\,dz$$

$$\frac{1}{\omega} = \frac{dJ}{dE} = \left(\frac{1}{2}+\frac{1}{n}\right)E^{-1}J$$

$$J\omega = \frac{2\,n}{n+2}\,E = \frac{1}{c}\,E \qquad \text{and} \qquad j\omega = \frac{1}{c}\,x. \tag{6}$$

For a box-potential (i. e., "$n = \infty$") it is seen that c has to be put equal to $\frac{1}{2}$ in eq. (6). For these potentials the distribution function y thus obeys the differential equation

$$x\,\frac{d^2y}{dx^2} + (c-x)\frac{dy}{dx} + ay = 0 \qquad \text{with} \qquad a = ck. \tag{7}$$

Exact solutions of Kramers' equation

The exact solution of eq. (7) is a confluent hypergeometric series[9]

$$y = {}_1F_1(-a, c; x) = 1 - \frac{a}{c}x - \frac{a(-a+1)}{c(c+1)}\frac{x^2}{2!} + \dots \tag{8}$$

and our result is therefore

$$\Phi = \sum_k b_k e^{-k\tau} e^{-x} {}_1F_1(-a, c; x). \tag{9}$$

The values of k which must be selected in the summation above are determined by the boundary condition: ${}_1F_1(-a, c; x^*) = 0$. The physical meaning of the condition: $\Phi = 0$ for $x \geqslant x^*$ is that the particle associated with the oscillating motion of the molecules considered is simply annihilated, when it—during its random motion—reaches the reduced energy x^*.

The eigenvalues $a = ck$ given by the equation

$${}_1F_1(-a, c; x) = 0 \tag{10}$$

lie very close to the integers 0, 1, 2, 3, . . . for large values of $x = \frac{D}{kT}$. Because of the factor $e^{-k\tau}$ in each term of eq. (9), the term corresponding to the smallest eigenvalue $a_0 \ll 1$ will be quite dominating, if only a certain time has elapsed since the system was "started" with some initial distribution, and the error made by setting Φ equal to this first term will therefore be completely negligible for reasonable values of x^* (say $x^* > 5$).

The reduced rate constant k_0 for the annihilation process—and for the chemical reaction—is defined by:

$$\frac{dN}{d\tau} = -k_0 N$$

where N is the total number of particles in the potential well

$$N = \int_0^{x^*} \Phi(x, \tau)\, dx.$$

It can therefore be calculated from the following expression in which all terms in the solution for Φ except the first have been neglected.

$$k_0 = \frac{-\dfrac{d}{d\tau}\displaystyle\int_0^{x^*} b_0 e^{\frac{a_0}{c}\tau} e^{-x} {}_1F_1(-a_0, c; x)\, dx}{\displaystyle\int_0^{x^*} b_0 e^{\frac{a_0\tau}{c}} e^{-x} {}_1F_1(-a_0, c; x)\, dx} = \frac{a_0}{c}. \tag{11}$$

The problem of calculating the rate constant is by eq. (11) reduced to the purely mathematical problem of finding the lowest value for a which satisfies (10).

If ${}_1F_1$ is Taylor-expanded in a_0, assuming that $a_0 \ll 1$, we obtain the following approximate solution of eq. (10) as ${}_1F_1(0, c; x) = 1$

$$\frac{1}{a_0} = \left(\frac{\partial\, {}_1F_1(a, c; x^*)}{\partial a}\right)_{a=0} = \frac{x^*}{c} + \frac{x^{*2}}{c(c+1)2} + \dots \tag{12}$$

By means of eq. (12) it is possible to evaluate a_0 directly as a function of x^* (method 3), but a simpler, although somewhat more approximate, formula can be found by using

$$\int_0^{x^*} \frac{{}_1F_1(1, c; x) - 1}{x}\, dx = \frac{x^*}{c} + \frac{x^{*2}}{c(c+1)2} + \dots$$
$$= \left(\frac{\partial\, {}_1F_1(a, c; x^*)}{\partial a}\right)_{a=0}.$$

The integration above is carried out by setting

$$\int \frac{{}_1F_1(1, c; x)}{x}\, dx = {}_1F_1(1, c, x)\,(a_0 + a_1 x^{-1} + \dots) + \text{const.}$$
$$= {}_1F_1(1, c; x)\, P(x^{-1}) + \text{const.}$$

and determining the coefficients $a_0, a_1, \dots$ in the polynomium P by differentiation

$${}_1F_1(1, c; x) = x\frac{\partial\, {}_1F_1}{\partial x} P + x\, {}_1F_1 \frac{dP}{dx}.$$

If at this place we substitute the asymptotic formula for ${}_1F_1(1, c; x)$[9], valid for $x \gg 1$

$${}_1F_1(1, c; x) = \frac{\Gamma(c)}{\Gamma(1)} e^x x^{1-c}$$

P can be determined to be

$$P = x^{-1} + cx^{-2} + c(c+1)x^{-3} + \dots$$

and in this way we obtain

$$\int_0^{x^*} \frac{{}_1F_1(1, c; x) - 1}{x}\, dx = \int_0^1 \frac{{}_1F_1(1, c; x) - 1}{x}\, dx + \int_1^{x^*} \frac{{}_1F_1(1, c; x)}{x}\, dx - \ln x^*$$

$$= \int_0^1 \frac{{}_1F_1(1, c; x) - 1}{x}\, dx - \ln x^* + \left[{}_1F_1(1, c; x) \frac{1}{x} \right]_1^{x^*}$$

$$= \Gamma(c)\, e^{x^*} x^{*-c} + 0\,(\ln x^*).$$

We have therefore obtained the following asymptotic formula

$$k = \frac{1}{\Gamma(c+1)}\, e^{-x^*} x^{*c} = \frac{1}{\Gamma(c+1)}\, e^{-\beta D} (\beta D)^c \tag{13}$$

which rapidly converges upon the exact result as the value of x increases. As mentioned in the introduction, this result is precisely what one would expect more intuitively, namely $k \propto \frac{1}{\omega(x^*)} x^* e^{-x^*}$.

The agreement between the k-values given by eq. (13) and those obtained by numerical solution of eq. (10) either by a machine method[10], which has been done for $c = 1$, or by other methods such as method 3, mentioned above, is fairly good for the higher values of x (see table 1).

The variational method

We now return to the general problem of solving the Kramers equation (3) without making assumptions about the form of the potential in which the particle moves. First of all we are interested in a method which allows a calculation of the smallest value of k for which Φ satisfies the boundary conditions, because this value is equal to the rate constant k. For that purpose a variational method is used. The method enables us to determine k-values only a little larger than the exact ones by approximating Φ with a trial function.

It is immediately observed that equation (4) is of the Sturm-Liouville type and that y satisfies the Sturm-Liouville boundary conditions:

$$y\, j\, e^{-x} \frac{dy}{dx} = 0 \text{ both for } x = 0 \ (j = 0) \text{ and for } x = x^* \ (y = 0).$$

Therefore

$$k_0 = \frac{-\int_0^{x^*} y \frac{d}{dx}\left(j\, e^{-x} \frac{dy}{dx} \right) dx}{\int_0^{x^*} y^2 \frac{1}{\omega} e^{-x}\, dx} = \frac{\int_0^{x^*} \left(\frac{dy}{dx} \right)^2 j(x)\, e^{-x}\, dx}{\int_0^{x^*} y^2 \frac{1}{\omega(x)} e^{-x}\, dx}.$$

TABLE 1.

Values for the rate constant k, in reduced units.

x^*	method	Potential $V = C\,\lvert q^n \rvert \left(n = \frac{2}{2c-1}\right)$			Morse potential
		$n = \infty,\ c = \frac{1}{2}$ box-potential	$n = 2,\ c = 1$ harmonic potential	$n = 1,\ c = \frac{3}{2}$ const. force potential	
2	1)	0,216	0,271	0,288	
	2)	0,249	0,348	0,463	0,414
	3)				
	4)		0,329		0,372
5	1)	0,0170	0,0337	0,0566	
	2)	0,0156	0,0288	0,0471	0,0388
	3)	0,0152			
	4)		0,0274		0,0345
10	1)	$1{,}62 \cdot 10^{-4}$	$4{,}54 \cdot 10^{-4}$	$10{,}8 \cdot 10^{-4}$	$6{,}21 \cdot 10^{-4}$
	2)	$1{,}54 \cdot 10^{-4}$	$4{,}09 \cdot 10^{-4}$	$9{,}28 \cdot 10^{-4}$	
	3)	$1{,}53 \cdot 10^{-4}$		$9{,}00 \cdot 10^{-4}$	
	4)		$4{,}02 \cdot 10^{-4}$		$5{,}86 \cdot 10^{-4}$
15	1)	$1{,}33 \cdot 10^{-6}$	$4{,}58 \cdot 10^{-6}$	$13.3 \cdot 10^{-6}$	
	2)				
	3)	$1{,}29 \cdot 10^{-6}$		$12{,}1 \cdot 10^{-6}$	
	4)		$4{,}26 \cdot 10^{-6}$		
20	1)	$1{,}04 \cdot 10^{-8}$	$4{,}12 \cdot 10^{-8}$	$13{,}9 \cdot 10^{-8}$	
	2)	$1{,}01 \cdot 10^{-8}$	$3{,}92 \cdot 10^{-8}$	$12{,}9 \cdot 10^{-8}$	$6{,}45 \cdot 10^{-8}$
	3)			$12{,}9 \cdot 10^{-8}$	
	4)		$3{,}90 \cdot 10^{-8}$		$6{,}45 \cdot 10^{-8}$

Method 1) is based on formula (13).

Method 2) is based on formula (17) using table 2.

Method 3) is based on formula (12).

The confluent hypergeometric series has been evaluated directly by means of a desk computer.

Method 4) are calculations on a digital computer.

The variational principle now guarantees that if—instead of the exact solution y—we substitute a "trial function" $Y(x)$ into this expression, a value k_0' comes out

$$k_0' = \frac{\int_0^{x^*} \left(\frac{dY}{dx}\right)^2 j(x)\, e^{-x}\, dx}{\int_0^{x^*} Y^2 \frac{1}{\omega(x)} e^{-x}\, dx} \tag{14}$$

which is larger than k_0. By varying the parameters in the trial function until k_0' attains it minimum value, we can therefore determine an approximate value for k_0.

If the denominator in eq. (14) is considered as a normalization constant for Y, this problem can be formulated as the problem of finding among all possible normalized functions for which $Y(x^*) = 0$ that function y which minimizes the integral

$$\int_0^{x^*} \left(\frac{dY}{dx}\right)^2 j(x)\, e^{-x}\, dx. \tag{15}$$

It is interesting to note that this integral is formally identical with the "generalized entropy production" discussed previously by one of us[11] in connection with ordinary diffusion. Therefore the variational principle can be considered formally as a case of the theorem of Prigogine stating that a stationary irreversible process is characterized by a minimal production of entropy.

If in eq. (14) we change to the new variable $X = x/x^*$, we obtain

$$k_0' = \frac{\int_0^{1} \left(\frac{dY}{dX}\right)^2 j(X)\, e^{-x^* X}\, dX}{x^{*2} \int_0^{1} Y^2 \frac{1}{\omega(X)} e^{-x^* X}\, dX}. \tag{16}$$

In the calculations of k_0'-values performed in this work we have used the trial function: $Y(X) = 1 - e^{x-x^*} = 1 - e^{x^*(X-1)}$, since a calculation for the harmonic potential with the use of a trial function including a parameter ξ, $Y = 1 - e^{\xi(x-x^*)}$ gave the lowest k_0'-value, when ξ was extremely close to the value 1. It should be noted that $y = 1 - e^{x-x^*}$ corresponds to a Ψ-function

$$\Psi = e^{-x} y = e^{-x} - e^{-x^*}.$$

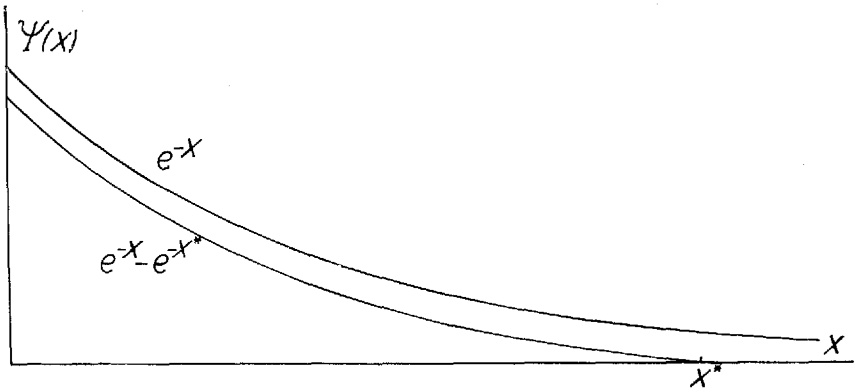

Fig. 1.

That is, except for a normalization factor it is simply an equilibrium distribution function from which a constant value e^{-x^*} has been substracted in order to make Ψ zero for $x = x^*$.

When this Y-function is substituted into eq. (16) we obtain

$$k_0' = e^{-2x^*} \frac{\int_0^1 e^{x^* X} j(X)\, dX}{\int_0^1 \frac{e^{-x^* X}}{\omega(X)} \left(1 + e^{2x^*(X-1)} - 2e^{x^*(X-1)}\right) dX}. \tag{17}$$

From this expression the values for the rate constant k listed in table 1 were calculated (Method 2).

Escape of a particle from a Morse potential

In order to obtain a better approximation to the true intramolecular potential for a diatomic molecule than the simple potentials discussed above and to check the above variational principle, we have investigated the escape of a particle from a Morse potential given by

$$V(r) = D(1 - e^{-r/\delta})^2$$

$$D = \frac{m}{2} \omega_0{}^2 \delta^2$$

r is the length of the molecule minus its equilibrium length, and ω_0 is the frequency of oscillations for very small energies, that is, the harmonic frequency. The magnitude of $1/\delta$ measures the degree of anharmonicity.

From this expression it follows that

$$J = \frac{1}{2\pi}\int p\,dr = \frac{2D}{\omega_0}\left(1 - \sqrt{1 - E/D}\right)$$

and

$$\omega = \omega_0 \sqrt{1 - E/D} = \omega_0 \sqrt{1 - x/x^*}$$

which when substituted in eq. (5) gives the equation

$$\frac{2}{x^*}\left[\sqrt{1-X} - (1-X)\right]\frac{d^2y}{dX^2} - 2\left[\sqrt{1-X} - (1-X) - \frac{1}{2x^*}\right]\frac{dy}{dX} + ky = 0.$$

Here we set $\sqrt{1-X} = 1 - u \; (0 \leqslant u \leqslant 1)$ and obtain

$$\frac{1}{2x^*}u(1-u)\frac{d^2y}{du^2} - \left[u(1-u)^2 - \frac{1}{2x^*}\right]\frac{dy}{du} + k(1-u)^2 y = 0. \tag{18}$$

This differential equation cannot be solved in terms of known functions, but by numerical integration the smallest value of k, for which a solution through the points $(u, y) = (0,1)$ and $(u, y) = (1,0)$ exists, can be found by a trial and error method. This was done on a digital computer and the results are listed in table 1.

In order to check the validity of the variational principle in the form developed above we have calculated the k_0' values given by eq. (17), where $j(X)$ and $\omega(X)$ for the Morse potential have been inserted. The expression used for these calculations is:

$$k_0' = \frac{1 - F(x^*)}{e^{x^*}G(x^*) + F(x^*) - 2} \approx 2x^* e^{-x^*} \text{ for large } x^*$$

in which

$$F(x^*) = \frac{1}{\sqrt{x^*}}\int_0^{\sqrt{x^*}} e^{-t^2}\,dt$$

and

$$G(x^*) = \frac{1}{\sqrt{x^*}}e^{-x^*}\int_0^{\sqrt{x^*}} e^{t^2}\,dt$$

$F(x^*)$ and $G(x^*)$ are listed in table 2. In the limit $x^* \gg 1$ F is asymptotically equal to $\frac{\sqrt{\pi}}{2x^*}$ and G asymptotically equal to $\frac{1}{2x^*}$. The expression for k_0' should be compared with that obtained for the harmonic potential:

$$k_0' = \frac{(x^*-1)e^{-x^*} + e^{-2x^*}}{1 - 2x^* e^{-x^*} - e^{-2x^*}} \approx x^* e^{-x^*} \text{ for large } x^*.$$

TABLE 2.

Values for the functions F and G

x^*	F	G
5	0,396	0,1157
10	0,280	0,0527
20	0,198	0,0256

Derivation of a diffusion equation in phase space

We have previously[7, 14] considered the Brownian motion of an oscillator coupled to a lattice which serves as a thermostat and shown that ϱ, the density in phase space of the system consisting of oscillator plus thermostat, satisfies the equation

$$\left.\begin{aligned}\frac{\partial \varrho}{\partial t} = \pi \lambda^2 \frac{L}{2\pi} \sum_{\nu} \int d\omega_f \frac{df}{d\omega_f} \Bigg\{ & \left(\frac{\partial}{\partial J_f} + \nu \frac{\partial}{\partial J}\right) | V_{\nu, f} |^2 \, \delta(\nu\omega + \omega_f) \left(\frac{\partial}{\partial J_f} + \nu \frac{\partial}{\partial J}\right) \\ & + \left(\frac{\partial}{\partial J_f} - \nu \frac{\partial}{\partial J}\right) | V_{\nu, f} |^2 \, \delta(\nu\omega - \omega_f) \left(\frac{\partial}{\partial J_f} - \nu \frac{\partial}{\partial J}\right) \Bigg\} \varrho \end{aligned}\right\} \quad (19)$$

in which J_f and ω_f are the action variable and the frequency of a lattice oscillation with wave number f, J and ω are the corresponding variables for the oscillator. $V_{\nu, f}$ is a Fourier coefficient of the non-harmonic interaction energy which will be defined below. In deriving this result it was assumed that ω is independent of J so that the Hamiltonian has the form

$$H = \sum_f \omega_f J_f + J + V.$$

We shall now see that precisely the same equation arises when ω depends on J, except that $V_{\nu, f}$ has to be defined slightly differently.

For the perturbing potential V we take

$$V(r) = \sum_n W(r - a_n) \, u_n$$

where u_n is the displacement of the n'th particle in the lattice, and $W(r - a_n)$ is the force exerted on the oscillator by an infinitesimal displacement of the n'th particle. This force of course depends on the stretching of the oscillator which is given by r. Expressing u_n in normal coordinates q_f we obtain

$$V = \sum_f V_f q_f e^{ifr}$$

with

$$V_f = \sum_n W(r - a_n)^{-if(r - a_n)}.$$

As an approximation we assume V_f to be independent of r for all values of f.

The equation for ϱ given above is derived from the spectrally decomposed Liouville equation, using the integration technique developed by BROUT and PRIGOGINE[12]. In order to apply this method the interaction potential V must be Fourier expanded on the angle variable α. This can be done quite simply in the case of a harmonic oscillator by using

$$r = r_0 \sin \alpha$$

and

$$e^{ifr_0 \sin \alpha} = \sum_{m=-\infty}^{\infty} J_m(fr_0)\, e^{im\alpha} \tag{20}$$

where J_m is the Bessel function of m'th order.

Using $q_f = q^0_{f+} e^{i\alpha_f} + q^0_{f-} e^{-i\alpha_f}$ one then obtains

$$V = \sum V_f q_f e^{ifr} = \sum_m \sum_f \left\{ V^+_{m,f}\, e^{i(\alpha_f + m\alpha)} + V^-_{m,f}\, e^{i(-\alpha_f + m\alpha)} \right\}$$

with

$$V^+_{m,f} = V_f q^0_{f+} J_m(fr_0)$$

$$V^-_{m,f} = V_f q^0_{f-} J_m(fr_0).$$

The squares of the absolute values of these Fourier coefficients are independent of the index + or − and are the quantities $|V_{\nu,f}|^2$ used above.

When the oscillator is not harmonic we still have $r = r_0(J)\,\Theta(\alpha)$ for the simple potentials we are going to consider. Here $\Theta(\alpha)$ is a periodic function with the property $|\Theta(\alpha)| \leqslant 1$. We now define the functions Y_m as

$$e^{ifr_0 \Theta(\alpha)} = \sum_{m=-\infty}^{\infty} Y_m(fr_0)\, e^{im\alpha} \tag{21}$$

and replace $J_m(fr_0)$ in the equations above by $Y_m(fr_0)$. When $|V_{\nu,f}|^2$ is redefined in this way, and it is assumed that $\omega = \omega(J)$ is a function of J, equation (1) now describes the evolution of ϱ for the system of an anharmonic oscillator in a lattice of harmonic oscillators.

We then use that

$$|V_{\nu,f}|^2 = |V_f|^2 \, |q_f|^2 \, Y^2_\nu(fr_0)$$

and

$$|q_f|^2 = \frac{J_f}{M^{(N)}\,\omega_f}$$

where $M^{(N)}$ is the total mass of the lattice.

Also, as is usual in calculations of this sort, we use the Peierls assumption

$$\frac{|V_f|^2}{\omega_f^2} = \text{constant}$$

and the Debye spectrum for the phonons

$$\frac{d\omega_f}{df} = c$$

where c is the velocity of sound in the crystal. Finally we assume that the crystal is in equilibrium, i. e., we set

$$\omega_f J_f = kT.$$

Under these assumptions the integration over ω_f is elementary because of the δ function, and the sum over ν in the equation for ϱ amounts to evaluating

$$\sum_{\nu=-\infty}^{+\infty} \nu^2 Y_\nu^2 \left(\nu \frac{\omega r_0}{c}\right).$$

For the case of a harmonic oscillator an analytical expression for the above sum has been found by SCHOTT[17], namely

$$\sum_{\nu=-\infty}^{+\infty} \nu^2 J_\nu{}^2(\nu z) = \frac{z^2(4+z^2)}{8(1-z^2)^{1/2}} \tag{22}$$

and since $z = r_0 \omega/c$ is small compared to one, the right hand side is replaced by $\frac{1}{2} z^2$.

In general an analytical expression for the sum $\sum\limits_\nu \nu^2 Y_\nu^2(\nu z)$ cannot be found, but we can find an approximate expression for the sum valid under the same conditions as above.

Expanding in powers of z we have

$$\sum_\nu \nu^2 Y_\nu^2(\nu z) = \sum_\nu \nu^2 Y_\nu^2(0) + 2z \sum_\nu \nu^3 Y_\nu(0) Y_\nu'(0)$$
$$+ z^2 \sum_\nu \nu^4 [Y_\nu'(0)^2 + Y_\nu(0) Y_\nu''(0)] + \ldots$$

From the definition of $Y_\nu(z)$ it is immediately seen that $Y_\nu(0) = \delta_{\nu,0}$ and therefore the above expansion reduces to

$$\sum_\nu \nu^2 Y_\nu^2(\nu z) = z^2 \sum \nu^4 Y_\nu'(0)^2 + 0(z^3).$$

Using the definition of $Y_\nu(z)$ and Parsevals theorem for the Fourier coefficients we have

$$\sum \nu^4 Y_\nu'(0)^2 = \frac{1}{2\pi}\int_{-\pi}^{\pi}(\theta''(\alpha))^2\, d\alpha$$

and therefore

$$\begin{aligned}\sum \nu^2 Y_\nu^2\left(\nu\frac{\omega r_0}{c}\right) &= \frac{\omega^2}{2\pi c^2}\int_{-\pi}^{\pi}(r''(\alpha))^2\, d\alpha \\ &= \frac{1}{2\pi c^2 m^2}\int_0^T (m\ddot{r}(t))^2\, dt \\ &= \frac{1}{c^2 m^2 \omega^2}\overline{\left(\frac{\partial V}{\partial r}\right)^2} \qquad (23)\end{aligned}$$

where the bar denotes time average.

With the same abbreviations as we have used before, i. e.,

$$\varkappa = \lambda^2 \frac{V_f^2}{\omega_f^2}$$

$$\mu = \frac{M^{(N)}}{L}$$

$$x = E\beta = \int \omega(J)\,\beta\, dJ$$

we have

$$\frac{\partial \Phi}{\partial t} = \frac{\varkappa\beta}{\mu c^3 m^2}\,\omega(x)\frac{\partial}{\partial x}\,\omega^{-1}(x)\overline{\left(\frac{\partial V}{\partial r}\right)^2}\left(1+\frac{\partial}{\partial x}\right)\Phi \qquad (24)$$

which deviates from the classical Kramers equation in that $J(x)$ has been replaced by (a constant times) $\omega^{-1}\overline{\left(\frac{\partial V}{\partial r}\right)^2}$. It is easily seen, for instance by using the virial theorem, that for a harmonic oscillator

$$\overline{\left(\frac{\partial V}{\partial r}\right)^2} = \gamma\beta x$$

where γ is the force constant, so that for this case we obtain the same result as previously, namely

$$\frac{\partial \Phi}{\partial t} = \eta\frac{\partial}{\partial x}\,x\left(1+\frac{\partial}{\partial x}\right)\Phi$$

with

$$\eta = \frac{\varkappa\gamma}{\mu c^3 m^2}.$$

To be able to use this formalism on non-harmonic oscillators we must first estimate how large an error in the rate constant we commit by replacing the right hand side of eq. (22) by $\frac{1}{2}z^2$. This is necessary because the validity of eq. (24) depends on a similar approximation.

Using the complete expression (22) in the master equation eq. (19) we find

$$\frac{\partial \Phi}{\partial t} = \eta \frac{\partial}{\partial x} x \frac{1 + \varepsilon x}{\sqrt{1 - \varepsilon x}} \left(1 + \frac{\partial}{\partial x}\right) \Phi$$

where ε is the ratio of kT to $\frac{1}{2}mc^2$, m being the mass of the particle and c the sound velocity.

Using the variational principle and the same trialfunction as above we find that for large values of x

$$k = x^* e^{-x^*} \left[1 + \frac{3}{2}\varepsilon x^* + \frac{7}{8}\varepsilon^2 x^{*2} + \ldots\right]$$

and since εx^* is smaller than one for all cases of interest this expression is permissible. Although the approximation obtained by replacing eq. (22) by $\frac{1}{2}z^2$ primarily is good when one only considers the Brownian motion of the molecule at low energies it is seen that the ratio between the correct rate constant and the approximate rate constant is only a factor 2–3 even when $\varepsilon x^* \approx 1/2$. The temperature dependence of the preexponential factor is of course somewhat different in the two expressions, but since this dependence is small anyway and not easily accessible experimentally this is of minor importance.

We can therefore presumably use eq. (24) derived above for estimating the influence of anharmonicities on the rate of escape of a particle from a potential minimum.

For the box-potential, which is zero for $|r| \leqslant l/2$, we interprete $\overline{\left(\frac{\partial V}{\partial r}\right)^2}$ as $\left(\overline{\left|\frac{\partial V}{\partial r}\right|}\right)^2 = 16\,E^2/l^2 = \frac{2\gamma}{D}E^2$, where γ is the spring constant for the equivalent harmonic potential i. e. the harmonic potential for which the stretching $l/2$ corresponds to the potential energy D.

We then get

$$\frac{\partial \Phi}{\partial t} = 2\,\eta x^{*-1} \sqrt{x} \frac{\partial}{\partial x} x^{3/2} \left(1 + \frac{\partial}{\partial x}\right) \Phi$$

and now η has the same meaning as above. Using the variational principle we get

$$k_0' = 2\,x^{*-1}\,\frac{x^* - \frac{3}{2}\,[1 - G(x^*)]}{2\,F(x^*)\,e^{x^*} + G(x^*) - 2}$$

or, in the asymptotic limit $x^* \to \infty$

$$k_0 = \frac{2}{\sqrt{\pi}}\,\eta\,\sqrt{x^*}\,e^{-x^*}.$$

This is precisely the same result as that obtained by Kramers' theory in the limit $x^* \to \infty$, in spite of the fact that the equations for Φ are completely different.

For the potential $C\,|r|$ we have $\left(\frac{\partial V}{\partial r}\right)^2 = C^2 = \frac{1}{2} D\gamma$ where γ is again the spring constant of the equivalent harmonic potential. We therefore have

$$\frac{\partial \Phi}{\partial t} = \frac{1}{2}\,\eta x^*\,\frac{1}{\sqrt{x}}\,\frac{\partial}{\partial x}\sqrt{x}\left(1 + \frac{\partial}{\partial x}\right)\Phi$$

and, using the variational principle, we get

$$k_0' = \frac{1}{2}\,\eta x^*\,\frac{e^{-x^*}\,[1 - G(x^*)]}{F(x^*) - e^{-x^*}\,G(x^*) - \frac{4}{3}\,x^*\,e^{-x^*}}$$

or, in the asymptotic limit

$$k_0 = \eta\,\frac{1}{\sqrt{\pi}}\,x^{*3/2}\,e^{-x^*}.$$

This result deviates only by a factor of $\frac{3}{4}$ from what one obtains from the theory of Kramers. We see therefore that for these simple anharmonic potentials the theory of Kramers and the more rigorous theory give practically the same results for the rate constants in the limit of large activation energy in spite of the fact that the equations for the density in phase space look quite different. This does not necessarily mean, however, that the result also would be almost identical for, for instance, the Morse potential, because in this case $r = r(\alpha, J)$ cannot be factorized, and therefore the short-cut used above cannot be applied.

Conclusion

The main result of the above calculations is that anharmonicities in the intramolecular potential changes the rate of a dissociation reaction by a factor which is approximately inversely proportional to the generalized frequency of the particle when its energy is equal to the dissociation-energy.

This only holds true for potentials of the form $C\,|\,r\,|^n$. For the Morse potential, for which the frequency goes to zero at the dissociation limit, the increase in rate over that for the harmonic potential is only a factor of two.

The result seems to be rather independent of whether one uses the theory of Kramers or a more refined theory. In the latter case however, owing to mathematical difficulties, only some of the simpler potentials could be treated, not the Morse potential.

The fact that the rate is increased when the frequency decreases with energy is well known. In the language of quantum mechanics it means that the rate is increased when the density of energy levels increases with the energy. It is remarkable, however, that the increase in rate obtained in this way for the Morse potential is far smaller than one should have expected. RICE[13], for instance, estimated that the anharmonicity in the Morse potential would speed up a dissociation reaction by a factor of twenty over that of a harmonic oscillator molecule. The most intuitive reason for this is probably to be sought in the fact that for potentials of the form $V = C\,|\,r\,|^n$ the anharmonicity is operative already at very low energies ($r \sim 0$) whereas the Morse potential is almost harmonic up to fairly high energies.

Although the results obtained here for the Morse potential using the Kramers theory conceivably could be changed somewhat by a more rigorous theory, we feel that the influence of anharmonicity in weak interaction theories has perhaps been somewhat overestimated in the past. Since hard core interactions play an important role in gasphase kinetics and no experimental result, to our knowledge, exists for dissociation of molecules interacting with phonons, it would be premature to try to compare with experiments at this stage.

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