Statistical Investigation of Dissociation Cross-Sections for Diatoms*

BY JAMES KECK

Avco-Everett Research Laboratory, 2385 Revere Beach Parkway,
Everett, Mass., U.S.A.

Received 1*st February*, 1962

An efficient statistical method for investigating the mechanism and rate of simple chemical reactions has been developed. The procedure involves the random selection of representative systems from the middle of the reaction zone, followed by numerical integration of the equations of motion in both directions to determine the complete course of the reaction. The approach has the important advantage over the usual one of sampling outside the reaction zone that the fraction of systems which react is tremendously increased. The method has been used to investigate the dissociation and recombination of H_2, O_2 and I_2 in collisions with argon at temperatures of 0·01 and 0·1 the dissociation temperature D/k. A total of 2400 systems were followed, approximately half of which resulted in a reaction. The cross-section for dissociation as a function of the internal energy H_{12} of the diatom was found to be proportional to $[1+(B-H_{12})/kT]^{-3\cdot5}$, where B is the height of the rotational barrier for the diatom.

In a previously published paper,[1] the author proposed a theory of chemical reaction rates by means of which it is possible to obtain a rigorous upper bound to the reaction rate which can be systematically lowered by a variational technique. Although similar theories were proposed more than 20 years ago by Wigner [2] and Horiuto,[3] they apparently failed to attract the attention of theoretical chemists and have been lost in the literature until recently. In these theories, the reacting system is represented by a point in an appropriate classical phase space and an upper bound to the reaction rate is obtained by calculating the flux of trajectories crossing a " trial " surface dividing the reactants from the products. The bound may then be lowered by adjusting the parameters which define the " trial " surface to produce the minimum crossing rate. The reason this procedure leads only to an upper bound for the reaction rate is that, although in principle there exists a class of surfaces which are crossed only once by any one trajectory, in practice the " trial " surfaces chosen will almost never belong to this class and may be crossed many times by single trajectories. Thus, in the calculations of the reaction rate we will have included some trajectories which do not react at all, as well as others which react only after multiple traversals of the " trial " surface.

The present work was initially undertaken to investigate the effect of multiple traversals of the " trial " surface on the calculation of the rate of dissociation and recombination of diatoms in collisions with noble gases carried out in ref. (1). The method involves the random sampling of phase-space trajectories crossing a " trial " surface tangent to the top of the rotational barrier for the diatom, followed by numerical integration of the classical equations of motion in both directions in time

---

* This work has been supported jointly by Headquarters, Ballistic Systems Division, Air Force Systems Command, United States Air Force, under Contract ≠AF04(694)-33 and Advanced Research Projects Agency, monitored by the Army Rocket and Guided Missile Agency, Army Ordnance Missile Command, United States Army, under Contract ≠DA-19-020-ORD-5476.

to determine the complete trajectories. Given the complete trajectories we can determine not only whether reaction occurred and the number of crossings of the " trial " surface involved, but also the dependence of the reaction probability on the initial configuration of the system. This latter possibility, which is made practical by the large fraction of trajectories which react, opens an extremely interesting field for investigation, the first results of which are the determinations of the dissociation cross-sections as a function of vibrational energy presented in fig. 6 of this paper.

MATHEMATICAL FORMULATION

Following the methods of ref. (1) an upper bound R_0 to the equilibrium rate of a chemical reaction A→B may be obtained in the form

$$R_0 = \int_{\mathbf{v}\,.\,\mathbf{n}>0}^{S} \rho_e(\mathbf{v}\,.\,\mathbf{n})\mathrm{d}\sigma, \tag{1}$$

where $\mathrm{d}\sigma$ is an element of the hypersurface S which divides the reactants A and products B, $\mathbf{n}$ is the unit normal to $\mathrm{d}\sigma$, $\mathbf{v}$ is the generalized velocity of a point in phase space and ρ_e is the equilibrium density of representative points.

To obtain a corresponding expression for the true rate we proceed as follows. Let $R(i,j)$ be the partial rate associated with trajectories which make i traversals of S in the direction of $\mathbf{n}$ and j traversals in the opposite direction. By definition,

$$R(i,j) = \int_{\mathbf{v}\,.\,\mathbf{n}>0}^{S(i,j)} \rho_e(\mathbf{v}\,.\,\mathbf{n})\mathrm{d}\sigma, \tag{2}$$

where $S(i,j)$ is that part of S crossed by trajectories in the class (i,j). Since the trajectories are continuous curves in phase space and S cannot have any " holes ", $R(i,j) \equiv 0$ unless $j = i, i\pm 1$. For a reaction to occur, the number of traversals of S which a trajectory makes in the direction of $\mathbf{n}$ must exceed the number it makes in the opposite direction. Hence, $j = i-1$ and the true reaction rate

$$R = \sum_i (i^{-1}) R(i,i-1), \tag{3}$$

where the factor i^{-1} has been introduced to correct for the fact that a single trajectory crossing $S(i,j)$ i times contributes i times to $R(i,j)$.

In general, it will not be possible to calculate $R(i,j)$ because the surfaces $S(i,j)$ are not known. However, we can obtain a statistical estimate $R(i,j)$ by numerical methods. To do this, we select a random sample of trajectories crossing S with a weight function proportional to the flux $\rho_e(\mathbf{v}\,.\,\mathbf{n})$. We then follow these trajectories through the reaction in both directions from S to determine their histories. The rate

$$R(i,j) = R_0 \lim_{N_0\to\infty} N(i,j)/N_0\,, \tag{4}$$

where N_0 is the number of trajectories followed and $N(i,j)$ is the number falling in the class (i,j).

In practice, the success of this procedure for investigating reaction rates depends on the fraction $N(i,i-1)/N_0$ of reacting trajectories being fairly large. It is here that the present approach gains an important advantage over similar ones which have been made in the past. By starting the calculation in the middle of the reaction zone rather than outside it as is the usual procedure, the fraction of reacting trajectories is tremendously increased and what was a prohibitive calculation in terms of machine-time becomes quite modest.

CALCULATIONS OF REACTION PROBABILITY

We have applied the method outlined above to the problem of estimating the equilibrium rates for the reactions

$$2H+A \rightleftharpoons H_2+A$$
$$2O+A \rightleftharpoons O_2+A$$
$$2I+A \rightleftharpoons I_2+A$$

for values of kT/D equal to 0·01 and 0·1.

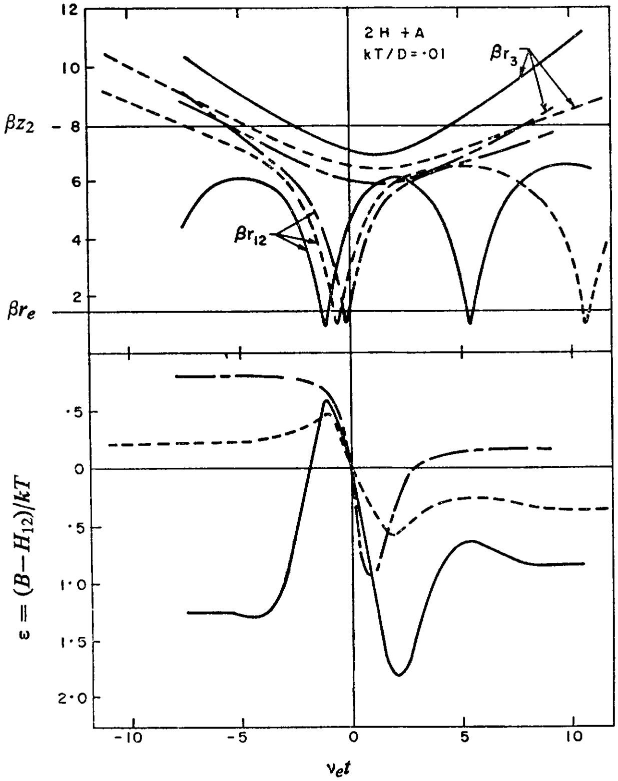

FIG. 1.—Typical trajectory histories for collisions involving 2H and A at $kT/D = 0·01$. Shown plotted in dimensionless form are the separation r_{12} of the H atoms, the separation r_3 of A from the centre of the 2H and the difference $(B-H_{12})$ between the instantaneous height of the rotational barrier and the energy of the 2H. $\nu_e = 1·3\times10^{14}\ \text{sec}^{-1}$ is the vibrational frequency of H_2 in the ground state, $\beta = 1·93\times10^{8}\ \text{cm}^{-1}$ is the decay constant appearing in the Morse potential, z_2 is the most probable position of the rotational barrier, and r_e is the equilibrium separation of H_2.

The calculations were carried out in the centre-of-mass system for the three particles. As in ref. (1) the interaction potential for the three-atom system was assumed to be the sum of the interaction potentials for the individual pairs of atoms. The Morse potential [4]

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

was used to represent the interaction between the atoms of the diatom and the Mason-Vanderslice potential [5]

$$V_{MV}(r) \approx D_{MV}\exp(-\beta_{MV}r)$$

was used to represent the interaction between an atom of the diatom and the argon atom. For simplicity, the Van der Waals attraction included in the calculations of ref. (1) was neglected in the present work.

The trajectories were started on a surface S^B tangent to the top of the rotational barrier for the diatom. The distribution functions for the initial co-ordinates and momenta were obtained by separating the eleven dimensional integral obtained from eqn. (1) as a product of integrals following the methods of ref. (1). The six coupled equations of motion were written in cartesian co-ordinates and integrated on an IBM 7090 computer using a 4th order Runge-Kutta method. The trajectories were followed in both directions from the initial point until the potential of interaction with the argon atom fell below $kT/100$. As a check on the interval size we required that changes in the total energy E and angular momentum L be limited to values $\Delta E \leq kT/100$ and $\Delta L \leq L/100$. The former condition was the more difficult to satisfy.

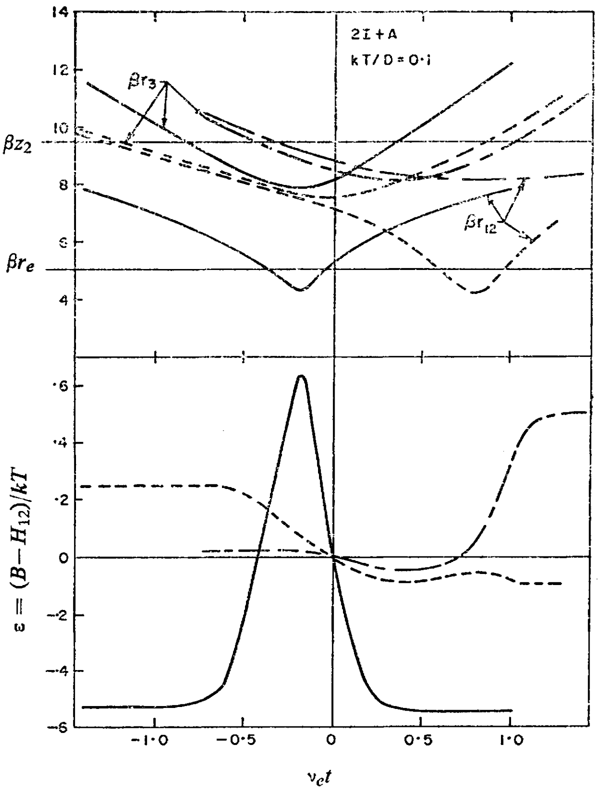

FIG. 2.—Typical trajectory plots for collisions involving 2I and A at $kT/D = 0{\cdot}1$. Shown plotted in dimensionless form are the separation r_{12} of the atoms, the separation r_3 of the A atom from the centre of the 2I, and the difference $(B - H_{12})$ between the energy of the 2I and the instantaneous height of the rotational barrier. $\nu_e = 6{\cdot}5 \times 10^{12}$ sec^{-1} is the vibrational frequency of I_2 in the ground state, $\beta = 1{\cdot}86 \times 10^8$ cm^{-1} is the decay constant appearing in the Morse potential, z_2 is the most probable position of the rotational barrier and r_e is the equilibrium separation of I_2.

For each case, 400 trajectories were followed making a total of 2400 trajectories and the total computer time involved was about 6 h. All of the 12 co-ordinates and momenta giving the relative positions and velocities of the three particles were printed out at the beginning and end of each trajectory. In addition, a tabulation was made

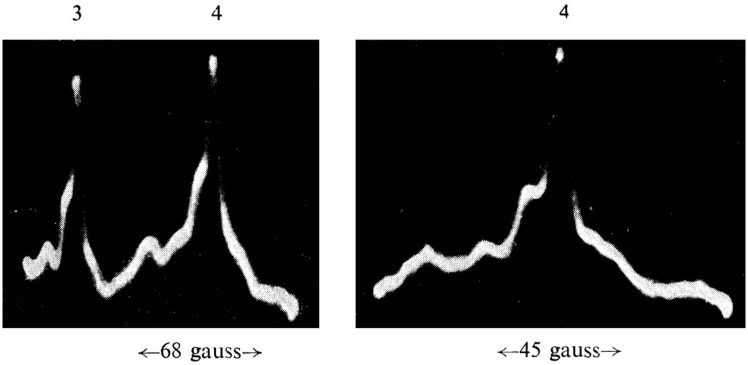

FIG. 1.—Section of paramagnetic resonance spectrum of 10^{-5} Mc in cubic ZnS.

of the internal energy H_{12} of the diatom, the height B of the rotational barrier for the diatom, the separation r_{12} of the atoms in the diatom, and the separation r_3 of the argon atom from the centre of the diatom. Examples of a few trajectory histories taken from this tabulation are shown in fig. 1 and 2. The cases chosen, 2H+A at $kT/D = 0{\cdot}01$, and 2I+A at $kT/D = 0{\cdot}1$, represent the two extremes in the ratio of the collision time to the vibrational period of the molecule. From the plots, one can form a general impression of the character of the particle motions, the duration of the collisions, and the excursions in the energy $(B-H_{12})$. Note that $(B-H_{12})$

TABLE 1.—DISTRIBUTION OF TRAJECTORIES WITH RESPECT TO CLASS OF REACTION AND NUMBER OF TRAVERSALS OF THE TRIAL SURFACE. THE PARAMETER $\theta = kT/D$

1*a* 2H+A

class	$\theta \mid i$	1	2	3	total
$N(f\mid i,i-1\mid b)$	·01	94	28	0	122
	·1	60	26	3	89
$N(f\mid i,i\mid f)$	·01	74	8	2	84
	·1	91	19	0	110
$N(b\mid i,i\mid b)$	·01	119	14	2	135
	·1	108	16	1	125
$N(b\mid i,i+1\mid f)$	·01	19	1	0	20
	·1	26	2	0	28
$N(\mathrm{d}E/\mathrm{d}t>0)$	·01	35	4	0	39
	·1	36	11	1	48
total	·01	341	55	4	400
	·1	321	74	5	400

1*b* 2O+A

class	$\theta \mid i$	1	2	3	total
$N(f\mid i,i-1\mid b)$	·01	146	33	2	181
	·1	128	31	0	159
$N(f\mid i,i\mid f)$	·01	81	4	0	85
	·1	77	14	0	91
$N(b\mid i,i\mid b)$	·01	94	8	0	102
	·1	100	6	0	106
$N(b\mid i,i+1\mid f)$	·01	15	0	0	15
	·1	13	1	0	14
$N(\mathrm{d}E/\mathrm{d}t>0)$	·01	12	5	0	17
	·1	28	2	0	30
total	·01	348	50	2	400
	·1	346	54	0	400

1*c* 2I+A

class	$\theta \mid i$	1	2		total
$N(f\mid i,i-1\mid b)$	·01	256	7	0	263
	·1	282	4	0	286
$N(f\mid i,i\mid f)$	·01	48	0	0	48
	·1	44	0	0	44
$N(b\mid i,i\mid b)$	·01	69	1	0	70
	·1	39	1	0	40
$N(b\mid i,i+1\mid f)$	·01	0	0	0	0
	·1	5	0	0	5
$N(\mathrm{d}E/\mathrm{d}t>0)$	·01	16	3	0	19
	·1	25	0	0	25
total	·01	389	11	0	400
	·1	395	5	0	400

approaches a constant value at the beginning and end of each trajectory indicating that the interaction with the third particle has indeed become negligible. Also note that the vibrational period for diatoms crossing the energy surface $(B-H_{12}) = 0$ is substantially larger than the ground-state vibrational period $\nu_e{}^1$.

In table 1, the results have been catalogued according to the type of transition involved and the number of traversals of the energy surface $(B-H_{12}) = 0$ in each direction. We have expanded the notation $N(i,j)$ of the preceding section to indicate the initial and final state of the diatom. Thus, $N(f\,|\,i,i-1\,|\,b)$ denotes the number of cases in which a trajectory went from a free state f to a bound state b with i crossings of $(B-H_{12}) = 0$ in the direction $f \rightarrow b$ and $i-1$ crossings in the direction $b \rightarrow f$. Note that there were a small number of cases denoted $N(\mathrm{d}\varepsilon/\mathrm{d}t > 0$ for which the initial traversal of the trial surface was in the wrong direction. This arose from an approximation made in separating the integral in eqn. (1) in which only the interaction between the third body and its nearest neighbour was taken into account. These cases are to be treated as non-reacting.

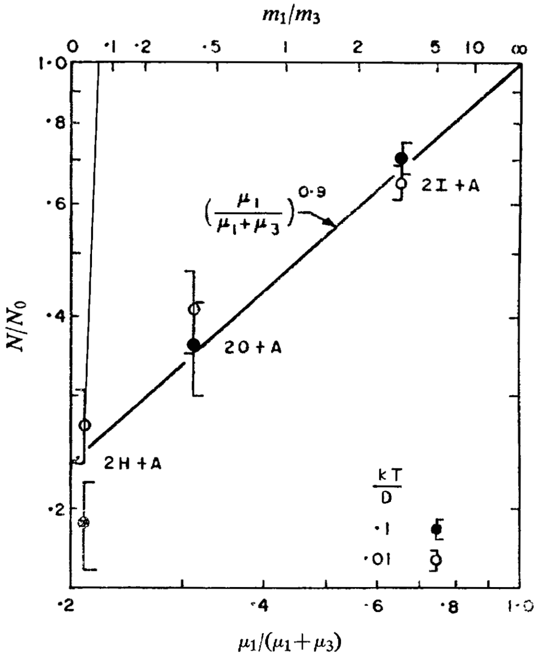

FIG. 3.—Ratio of number N of reacting trajectories to total number N_0 followed as a function of the ratio $\mu_{12}/(\mu_3+\mu_{12})$, where μ_{12} is the reduced mass of the diatom and μ_3 is the reduced mass for the collision. The upper scale shows the ratio of the mass m_1 of an atom of the diatom to the mass m_3 of the third body.

A number of interesting features are immediately apparent in table 1. First, and most welcome, is the large number of cases in which a reaction occurred. This implies that our original estimates of the rates based on the variational theory were not far wrong. Secondly, the number of trajectories which cross the trial surface more than once in each direction decreases rapidly as the number of crossings increases. Thirdly, within the statistical accuracy of the data there is very little indication of a temperature dependence in the results. Finally, there is a relatively weak dependence of the reaction probability on the mass of the recombining atoms.

In fig. 3 the fraction of reacting trajectories

$$N/N_0 = N_0^{-1}\sum_i (i^{-1})N(f\,|\,i,i-1\,|\,b) \tag{5}$$

is plotted as a function of $\mu_{12}/(\mu_{12}+\mu_3)$, where μ_{12} is the reduced mass of the diatom and μ_3 is the reduced mass of the argon and diatom. The data can be represented by the empirical equation

$$N/N_0 = [\mu_{12}/(\mu_{12}+\mu_3)]^{0\cdot 9}. \tag{6}$$

Although the present results give no indication of the dependence of the reaction rate on the mass of the " third body ", there is some evidence in the comparison of theory and experiment made in table 1 of ref. (1) which suggests that when the " third body " is lighter than the reacting atoms the recombination probability is near unity. Eqn. (6) is in accord with this suggestion.

DISSOCIATION CROSS-SECTION

As a result of the relatively large fraction of reactions occurring, it is possible to obtain information on the reaction probability as a function of conditions in the initial and final states of the system. Our first effort in this direction has been to investigate the number of reactions as a function of the energy of the bound state of the diatom. The results are shown in table 2 where we have tabulated the number of cases ΔN in which the ratio $\varepsilon = (B-H_{12})/kT$ falls between the values given in the first column. When correlated in this manner, the distribution exhibits very little mass or temperature dependence.

TABLE 2.—DISTRIBUTION OF REACTING TRAJECTORIES WITH RESPECT TO THE PARAMETER $\varepsilon = (B-H_{12})/kT$. THE PARAMETER $\theta = kT/D$

case	2H+A		2O+A		2I+A	
$\varepsilon \mid \theta$	·01	0·1	·01	0·1	·01	0·1
0·0-0·25	42	47	75	67	143	145
0·25-0·50	23	11	27	22	44	50
0·50-1·0	16	5	30	23	30	51
1·0-2·0	8	9	16	20	23	25
2·0-4·0	8	2	9	10	13	11
4·0-∞	11	0	6	1	6	2
N	108	74	163	143	259	284

The data in table 2 may be used to estimate the cross-section $\sigma(\varepsilon)$ for the dissociation of a diatom as a function of the parameter $\varepsilon = (B-H_{12})/kT$. To do this, we simply equate the differential reaction rate

$$\frac{\mathrm{d}R}{\mathrm{d}\varepsilon} \approx \frac{R_0}{N_0}\left(\frac{\Delta N}{\Delta \varepsilon}\right) = \left(\frac{N}{N_0}\right)\left(\frac{\Delta N}{N\Delta \varepsilon}\right) k_r K_e [\mathrm{X}_2][\mathrm{A}], \tag{7}$$

given by the present theory to the corresponding expression which defines the cross-section,

$$\begin{aligned} \frac{\mathrm{d}R}{\mathrm{d}\varepsilon} &= \sigma(\varepsilon)\frac{\mathrm{d}[\mathrm{X}_2]}{\mathrm{d}\varepsilon}\int_{\varepsilon}^{\infty} v_3 \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}\varepsilon_3}\mathrm{d}\varepsilon_3 \\ &= \sigma(\varepsilon)\frac{\mathrm{d}[\mathrm{X}_2]}{\mathrm{d}\varepsilon}[\mathrm{A}]\left(\frac{8kT}{\pi\mu_3}\right)^{\frac{1}{2}}(1+\varepsilon)\mathrm{e}^{-\varepsilon}, \end{aligned} \tag{8}$$

to obtain

$$\sigma(\varepsilon) \approx \left(\frac{N}{N_0}\right)\left(\frac{\Delta N}{N\Delta\varepsilon}\right) k_r K_e \Big/ \frac{\mathrm{d}\ln[\mathrm{X}_2]}{\mathrm{d}\varepsilon}\left(\frac{8kT}{\pi\mu_3}\right)^{\frac{1}{2}}(1+\varepsilon)\mathrm{e}^{-\varepsilon}, \tag{9}$$

where $[X_2]$ and $[A]$ are respectively the concentrations of diatoms and argon atoms, K_e is the equilibrium constant for the reaction $X_2 + A \rightleftharpoons 2X + A$, k_r is the recombination rate constant given by eqn. (45) in ref. (1), v_3 is the relative velocity of X_2 and A and $\varepsilon_3 = \mu_3 v_3^2/2kT$. For a rotating Morse oscillator, the factor

$$\frac{\mathrm{d}\ln[X_2]}{\mathrm{d}\varepsilon} \approx \frac{kT}{h\nu_e}\left[1-\exp\left(-\frac{h\nu_e}{kT}\right)\right]\left(\frac{\nu_e}{\nu}\right)\left(\frac{z_2}{r_e}\right)^2 \exp\left(-\frac{D}{kT}+\varepsilon\right), \tag{10}$$

where ν is the frequency of the rotating oscillator in the state $(B-H_{12})/kT = \varepsilon$, and z_2 is the most probable position of the rotational maximum which may be obtained from curves in the appendix of ref. (1).

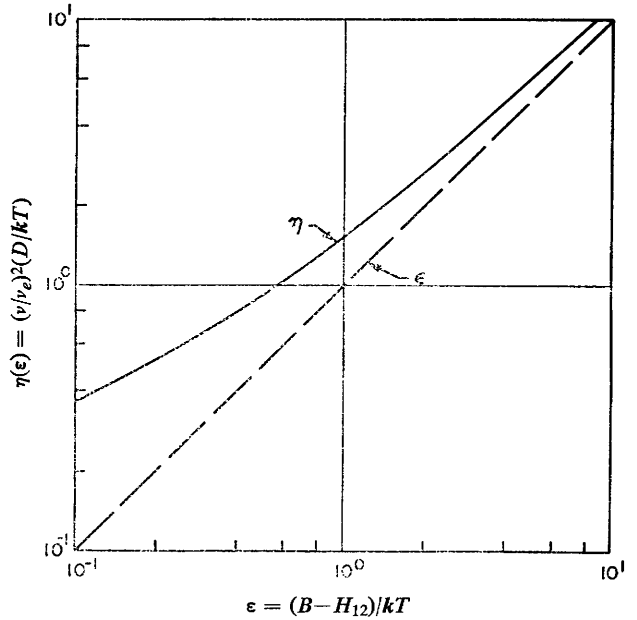

FIG. 4.—Curve of $\eta = (\nu/\nu_e)^2 D/kT$ as a function of the parameter ε. The curve is approximately valid for $1 < \beta r_e < 9$ and $0{\cdot}01 < kT/D < 0{\cdot}1$. For large ε, η is asymptotic to ε.

Combining eqn. (6), (9) and (10) we obtain

$$\sigma(\varepsilon) \approx \sigma_0\left(\frac{\Delta N}{N\Delta\varepsilon}\right)\frac{\eta^{\frac{1}{2}}}{(1+\varepsilon)}, \tag{11}$$

where $\eta = (\nu/\nu_e)^2 D/kT$ is shown plotted in fig. 4 as a function of ε and σ_0 is a cross-section of the order of 10^{-15} cm^2 which may be expressed in terms of parameters defined in ref. (1) as

$$\sigma_0 = \sqrt{\pi}a_{1-}^2\beta(z_2-z_1)\left(\frac{\mu_{12}}{\mu_{12}+\mu_3}\right)^{0\cdot 9}\left(\frac{\mu_3}{\mu_{12}}\right)^{\frac{1}{2}}\tfrac{1}{4}[F_p^{1-}+F_l^{1-}]\times\left[1-\exp\left(-\frac{B_m}{kT}\right)\right]. \tag{12}$$

The quantity $[F_p^{1-}+F_l^{1-}]/4$ which must be obtained by numerical methods is plotted in fig. 5 for the cases of interest here. The ratio $\sigma(\varepsilon)/\sigma_0$ computed from eqn. (11) using the data in table 2 is shown as a function of the parameter $(1+\varepsilon)$ in fig. 6. Within the statistical accuracy of the data, all the points can be fitted by the empirical equation

$$\sigma(\varepsilon)/\sigma_0 = 1{\cdot}5(1+\varepsilon)^{-3\cdot 5}. \tag{13}$$

Whether or not this particular functional form has any basic significance is not clear to the author. However, it does seem somewhat remarkable that the results which

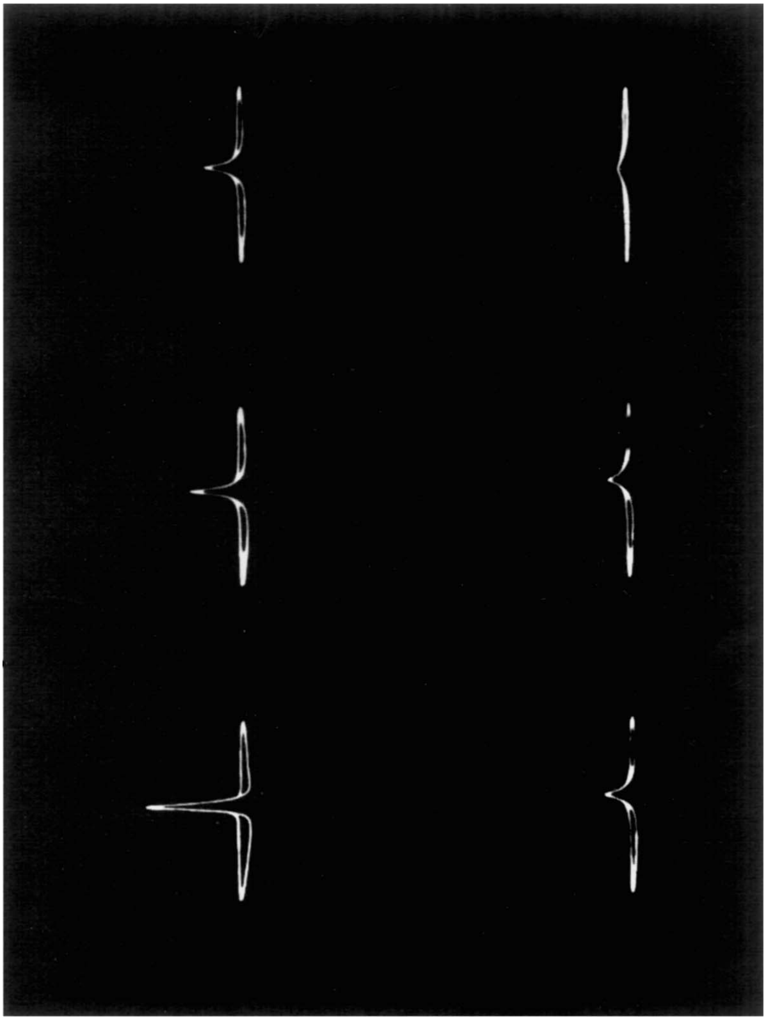

FIG. 3.

[*To face page* 180.

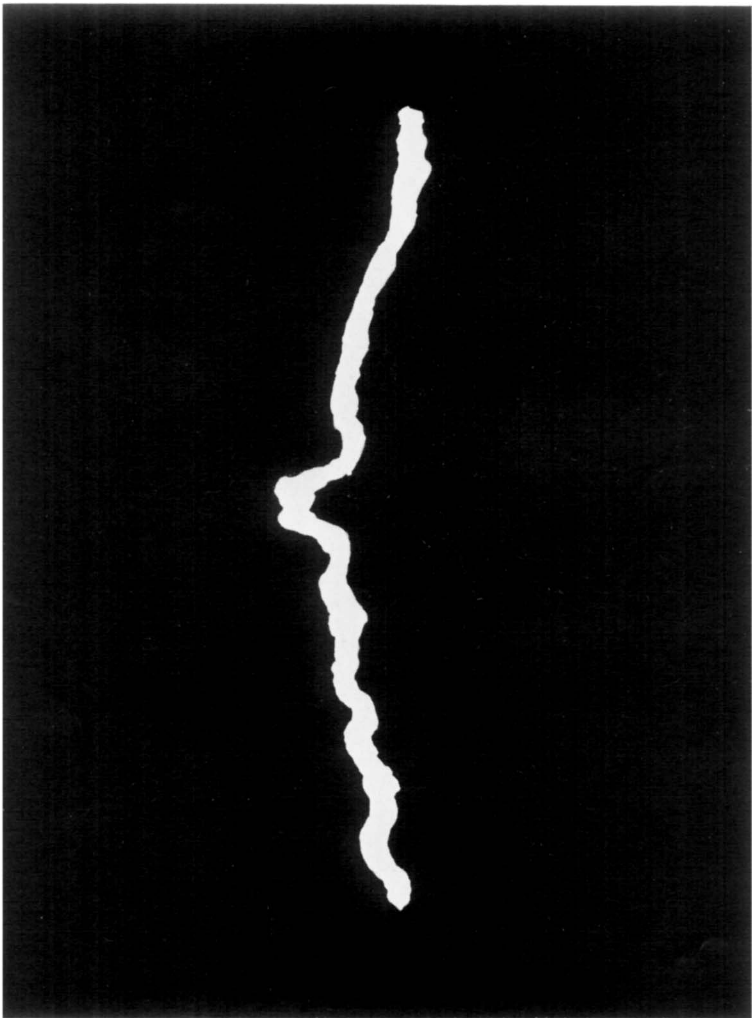

FIG. 4.

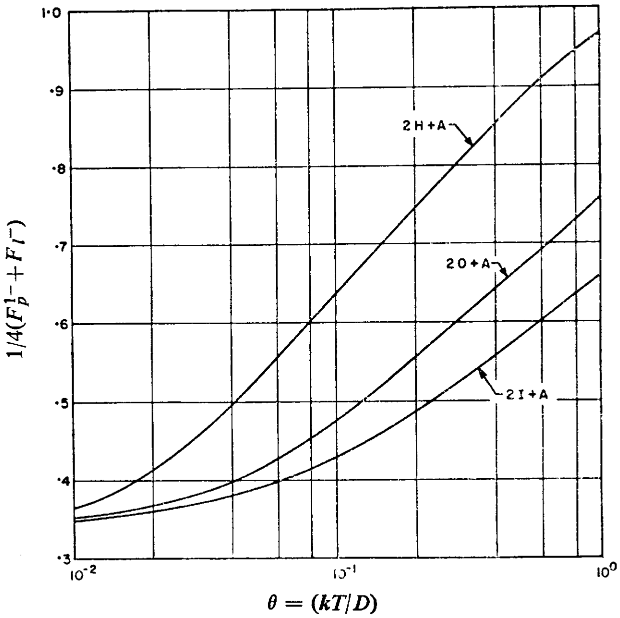

FIG. 5.—Curve of the function $(F_p^{1-}+F_l^{1-})/4$ required for computing dissociation cross-section from eqn. (12).

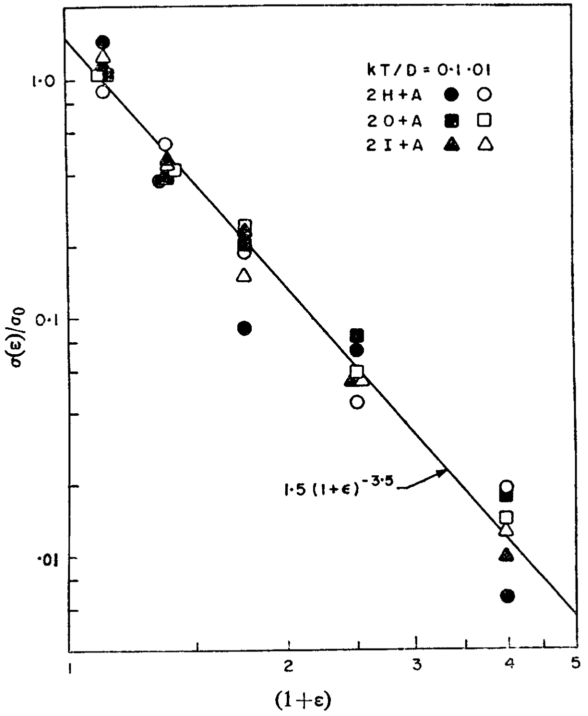

FIG. 6.—Calculated dissociation cross-sections as a function of $1+\varepsilon$. The reference cross-section σ_0 is defined in eqn. (12) and $\varepsilon = (B-H_{12})/kT$ where B is the height of the rotational maximum and H_{12} is the internal energy of the molecule. The scatter of the points about the line is compatible with the statistical errors involved.

span so wide a range of conditions can be correlated in so simple a manner. It should be noted that $(1+\varepsilon)$ is the mean energy transferred to the diatom divided by kT.

DISCUSSION

One of the fundamental reasons for our interest in the dissociation cross-section $\sigma(\varepsilon)$ is that it is independent of the assumption of equilibrium in the vibrational degree of freedom of the diatom. This is important for practical applications since it is virtually certain that during the process of dissociation or recombination in any experimental situation the vibrational states near the dissociation limit will be out of equilibrium. Unfortunately, direct observation of $\sigma(\varepsilon)$ will probably be extremely difficult. It is most likely that $\sigma(\varepsilon)$ will be observable only through its influence on the overall dissociation rate. In this connection a theory of coupled vibration and dissociation is being developed by some of the author's colleagues and will be published shortly.

With respect to the integrated reaction rate, the present work produces little change in the comparison between theory and experiment made in ref. (1). The theory predicts the experimental rates at room temperature well but overestimates the rates at high temperatures by a factor of about 5. The mass dependence of the reaction probability uncovered in the present work should slightly improve the correlation of the experiments shown in fig. 15 of ref. (1). It should also make possible correlation of recent data on the dissociation of H_2.

Since the theory developed here has the potential of giving considerable detail about the mechanics of simple chemical reactions, a restatement of the assumptions which have been made is well worth-while. The most fundamental of these is, of course, that classical mechanics is valid. The main argument here is based on a comparison of the reduced wavelength $\lambda\!\!\!^{-} = \hbar/(2MkT)^{\frac{1}{2}}$ for the heavy particles with the characteristic distance $\alpha_0 \approx 0{\cdot}5$ Å over which appreciable changes in force occur. The ratio

$$\lambda\!\!\!^{-}/\alpha_0 = (m_e/M)^{\frac{1}{2}}(R/kT)^{\frac{1}{2}} = (86/AT)^{\frac{1}{2}},$$

where m_e is the electron mass, R is the Rydberg energy, and A is the atomic mass. It can be seen that even for hydrogen at room temperature $\lambda\!\!\!^{-}/\alpha_0 \sim \frac{1}{2}$, while for all heavier molecules and higher temperatures it is substantially less. This implies that it should be possible to describe the particles by reasonably well-defined wave packets which will follow the classical orbits. The second assumption of importance is that the forces between the particles can be uniquely related to their positions and velocities. This requires that electronic transitions do not occur during the course of the collision and is related to the validity of the Born-Oppenheimer separation in chemistry. The final assumption is that the potential can be described as the sum of the interactions between pairs. While this affects the numerical results, it is not basic to the theory which can be used with any potential. In fact, the coupling of theory and experiment may well be useful for obtaining information about the nature of many-body interactions.

The author wishes to acknowledge the important contributions made to this work by Benjamin Woznik who blocked out the original IBM programme, Kendrick Ownby who made it work, and Anna Manzi who is currently assisting with the calculations.

[1] Keck, *J. Chem. Physics*, 1960, **32**, 1035.
[2] Wigner, *J. Chem. Physics*, 1937, **5**, 720.
[3] Horiuto, *Bull. Chem. Soc. Japan*, 1938, **13**, 210.
[4] Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand, New York, 1950).
[5] Mason and Vanderslice, *J. Chem. Physics*, 1958, **28**, 432.