vector; in this way, the two solutions merged satisfactorily into each other and did not give rise to spurious discontinuities in derived quantities, such as the rate constant or the entropy, in the region around 10^{-6} sec.

We end with a few remarks on the eigenvalues of this system of equations and the problem of the strict maintenance of particle conservation. The matrix $\mathbf{H}'(t)$ (corresponding to eq 20) has $(n + 2)$ eigenvalues (D'_0 to $D'_{(n+1)}$), one of which ($D'_{(n+1)}$) is necessarily zero by virtue of the right-most column of (26) being zero. It is usually assumed that the zero eigenvalue is needed to confer conservation of particles on the system. However, in our formulation this is not so; $D'_{(n+1)}$ is zero only because state $(n + 1)$ is inaccessible by a direct jump from any of the bound states; all transitions from $i \rightarrow (n + 1)$ have to go *via* the state n. To give an extreme example, suppose that eq 8–11 were interleaved by equations representing transitions to nonexistent states, all having zero probability for transition to real states. The master equation would then have a zero eigenvalue for each such state introduced; these zeros do not constitute a sufficient criterion to guarantee conservation of X particles in the normal sense, and we call them inaccessibility zeros. Furthermore, it is readily seen that eq 20a is *stochastic in form*, so that D_n of $\mathbf{H}(t)$ is also zero—but eq 20a does not conserve particles until the additional normalization of $\xi(t)$ is invoked through (12a)! Thus, we conclude that meticulous consideration has to be given to the problem of particle conservation; otherwise derived quantities like the rate constant or the rate of entropy production are quite meaningless. The remaining eigenvalues of the system (D_0 to $D_{(n-1)}$) are all negative and well-spaced, and all except one, *i.e.*, D_0 to $D_{(n-2)}$, have absolute magnitudes in the range 10^{11}–10^6 sec^{-1} with negligible time dependence; the last one, $D_{(n-1)}$, however, is quite time dependent, and rises from about -0.014 sec^{-1} at short times, through about -0.1 sec^{-1} at 1% reaction to about -3.5 sec^{-1} at equilibrium. Its behavior in recombination is complementary; near-complete dissociation, $D_{(n-1)}$, has a value of about -430 sec^{-1}, passing through about -140 sec^{-1} at 65% recombined, and, of course, approaching -3.5 sec^{-1} as equilibrium is reached.

The Master Equation for the Dissociation of a Dilute Diatomic Gas.[1] II. Application to the Dissociation of Hydrogen

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Abstract: The master equation, as described in part I of this series, is solved numerically for the dissociation of H_2 diluted in He, and also for the reverse reaction, the recombination of H atoms, using an assumed set of transition probabilities. In both processes, it is found that the total entropy is a *completely monotonic* function of the time; *i.e.*, successive derivatives d^nS/dt^n alternate in sign. Once the transient period is over, the phenomenological rate constants for both dissociation and recombination remain virtually independent of time and conform accurately to the rate-quotient law; there are, however, some conditions attached to this statement if integrated rate constants are used.

A. Dissociation

1. The Model. The hypothetical experiment simulated in this calculation is the following. A mixture consisting of 3.5×10^{16} molecules/cc of H_2 diluted in 3.5×10^{19} atoms/cc of He is heated instantaneously by a shock wave from an initial temperature of 0°K to a temperature T_0' near 2000°K. We focus our attention on a particular volume V of the gas and assume that, after the initial heating process, there is no transfer of matter or energy in or out of this volume. The system is therefore closed, and the reaction occurs at constant volume (the real process takes place at constant enthalpy, but the error introduced here is minimal[2]). It is assumed that one can imagine a time $t = 0$ at which the translational and rotational temperature of the gas is T_0' but the vibrational temperature is still 0°K. In the preceding paper,[3] we considered formally the more general case where the rotational degrees of freedom would still be those appropriate to 0°K at $t = 0$, but this still presents too formidable a computing problem. The hydrogen molecule has 301 bound rotation–vibration levels.[4] Thus one would have to solve a master equation of order 302 which is beyond our present capabilities; one would also need to know approximate transition probabilities among all these levels, and, as yet, we have no firm feeling for the way in which probabilities involving simultaneous changes of v and J will depend on $(\Delta v + \Delta J)$ and T. However, since the translational–rotational relaxation is very much more rapid than translational–vibrational relaxation,[5] even for H_2, a meaningful calculation can still be done by assuming that the translational and rotational degrees of freedom are always in equilibrium with each other, and simply

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(1) Research supported by the Defence Research Board of Canada (Grant No. 9550-35) and the National Research Council of Canada.

(2) C. T. Hsu and L. D. McMillen, *Phys. Fluids*, **11**, 2148 (1968).

(3) Part I: V. A. LoDato, D. L. S. McElwain, and H. O. Pritchard, **91**, 7688 (1969). Equations in this paper are referred to by a I preceding the equation number.

(4) T. G. Waech and R. B. Bernstein, *J. Chem. Phys.*, **46**, 4905 (1967).

(5) H. O. Pritchard in "Transfer and Storage of Energy," Vol. 2, John Wiley & Sons, Inc., London, 1969, pp 368–389.

Table I. The Hydrogen Molecule Vibrational Energy Levels and Equilibrium Population Distribution Function for $N = 3.5 \times 10^{6}$ molecules/cc at 2000°K

State i	$-\epsilon_i$, cm^{-1}	$\tilde{x}_i = \tilde{n}_i/N$
$v = 0$	36,117.42	9.416×10^{-1}
$v = 1$	31,955.35	4.715×10^{-2}
$v = 2$	28,028.56	2.797×10^{-3}
$v = 3$	24,332.02	1.958×10^{-4}
$v = 4$	20,863.18	1.614×10^{-5}
$v = 5$	17,620.89	1.567×10^{-6}
$v = 6$	14,606.37	1.791×10^{-7}
$v = 7$	11,823.57	2.420×10^{-8}
$v = 8$	9,279.92	3.882×10^{-9}
$v = 9$	6,986.57	7.457×10^{-10}
$v = 10$	4,959.98	1.735×10^{-10}
$v = 11$	3,223.02	4.974×10^{-11}
$v = 12$	1,807.61	1.797×10^{-11}
$v = 13$	758.72	8.449×10^{-12}
$v = 14$	138.71	5.409×10^{-12}
Pairs	...	5.309×10^{-9}
Atoms	...	8.252×10^{-3} [a]

[a] The fraction of molecules dissociated; *cf.* eq I(12).

concentrating on the vibrational and chemical aspects of the relaxation process. Of course, one loses some of the fine details peculiar to the H_2 problem, those associated with nuclear-spin statistics, and one avoids some of the complications arising from high rotational excitation, *i.e.*, the metastable states, tunneling, and centrifugal dissociation. Nevertheless, the calculations we have performed still reproduce, in our opinion, the main features of the dissociation process for a general diatomic molecule under highly dilute conditions.

The vibrational energy levels in H_2, which are taken from Poll and Karl,[6] are listed in Table I together with the population distribution function $\tilde{x}_i = \tilde{n}_i/N$ for the temperature 2000°K. The fractional concentration of dissociated molecules $\tilde{x}_{(n+1)}$ is derived from the equilibrium constant $K = 9.612 \times 10^{12}$ (molecules/cc) for the dissociation reaction,[7] and the fractional concentration of latent pairs $\tilde{x}_n$ follows from the equilibrium constant $\lambda = 5.569 \times 10^{-22}$ (cc/pair) calculated by Rush and Pritchard[8] [*cf.* eq I(3)]. Table II lists the assumed set of transition probabilities used in this calculation. With the exception of a more realistic choice for the $\bar{W}_{ni}$, they are like those used in our earlier work,[8,9] having been estimated crudely by perturbation methods;[10] however, since diatomics in general all exhibit the same kind of behavior in shock dissociations,[3] clearly this behavior cannot depend too critically on the individual transition probabilities, and it seems likely that if the chosen set embodies the right kind of interrelationships, the correct kinetic patterns should be reproduced.[11] To begin the calculation, the upper half of the P_{ij} matrix was read into the computer with two-decimal place precision and multiplied by $[\mathrm{He}]Z = 5.15 \times 10^{10}$ collisions per H_2 molecule per second to give the $[\mathrm{M}]W_{ij}$ of eq I(18). The lower half of $[\mathrm{M}]W_{ij}$ was then calculated from the detailed-balance relations I(14) to double-length (16-decimal place) accuracy, and the diagonal elements of $\mathbf{A}_{00}$ and $\mathbf{A}_{11}$ were then calculated in double length using eq I(18). It was found necessary to maintain this strict adherence to detailed balancing and conservation [eq I(19)]; otherwise the solutions inevitably failed to converge in the interesting time range or were unacceptable for other reasons.

A further minor approximation is introduced at this point. The whole of the data in Tables I and II and the $\mathbf{A}$ matrices derived therefrom correspond to a temperature of exactly 2000°K; with the mixture we have chosen, T_0' differs from this by about 0.5°K, and the translational–rotational temperature of the gas falls by this amount as the reaction proceeds. We have assumed that over this range of 0.5°K, the temperature dependence of Z, λ, and all the W_{ij} can be neglected; for less dilute mixtures, expanding flows, and recombination at low temperatures or when radiation is important, this approximation [eq I(22a) and I(28)] would be less acceptable.

2. The Relaxation. The results of these calculations are shown in the form of $\xi(t)$ as a function of t in Table III; this is divided into two sections (reflecting a difference in the method of calculation), Table III(a) relating to what is essentially the vibrational part of the relaxation and Table III(b) showing the chemical part of the process. In the latter part of the calculation, no difficulty was experienced in obtaining convergent solutions (even for times well in excess of those shown in Table III), and if the trial value of $\xi_n(t)$ was of the right order of magnitude, usually some 6–20 cycles were needed, each cycle took about 10 sec on an IBM 360/50.

The principal features of the relaxation are a very rapid equilibration among the first ten vibrational energy levels, followed by a relatively slow approach to the final equilibrium. In experimental studies, it is usually assumed[12,13] that the vibrational levels relax more or less completely before dissociation commences; since the populations of levels $v = 10$–14 only amount altogether to about 10^{-10} of the molecules present, the validity of this assumption is amply confirmed. Additionally, in a real shock wave, which is not instantaneous, this process seems to take about 1 μsec.[14] Once the transient period[15] is over, levels $v = 0$–9 remain essentially in equilibrium with each other, with populations approaching their equilibrium values monotonically from above; on the other hand, levels $v = 10$–14 and the continuum are always underpopulated, approaching their final equilibrium populations from below. Thus, with this particular set of assumed probabilities, the idea of a bottleneck[10,11] around $v = 9$ or 10 seems well established. It is also apparent that the populations of levels $v = 10$–14 execute one small oscillation in the early stages of the reaction, before the back-reaction becomes important, and during this period the main feature of the process appears to be that molecules dissociate from these levels just as quickly as

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(6) J. D. Poll and G. Karl, *Can. J. Phys.*, **44**, 1467 (1966).

(7) "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1965.

(8) D. G. Rush and H. O. Pritchard, Eleventh Symposium (International) on Combustion, Berkeley, Calif., 1967, p 13.

(9) D. G. Rush, Ph.D. Thesis, University of Manchester, Manchester, England, 1964.

(10) H. O. Pritchard, *J. Phys. Chem.*, **65**, 504 (1961).

(11) We have carried out auxiliary calculations in which some of the probabilities were varied from those in Table II by as much as $10^{\pm 4}$; while the actual rates of relaxation were affected, and the departures from equilibrium shown in Table III were more or less exaggerated, the general qualitative pattern exhibited in Table III persisted. Thus, our contention that the *nature* of the relaxation is dominated by statistical mechanics rather than the probabilities seems to be reasonably supported.

(12) H. O. Pritchard, *Quart. Rev.* (London), **14**, 46 (1960).

(13) J. P. Appleton, M. Steinberg, and D. J. Liquornik, *J. Chem. Phys.*, **48**, 599 (1968).

(14) I. R. Hurle, ref 8, p 827.

(15) B. Widom, *Science*, **148**, 1555 (1965).

they can be supplied from below; *in a strictly limited sense*, one could interpret this as representing a "steady state" (*cf.*, however, footnote 19).

3. Entropies. The results presented in Table III make it possible to calculate the entropy changes taking place during the relaxation. The entropy at any time t is taken to be

$$S(t) = S^{\mathrm{He}}{}_{\mathrm{trans}}(t) + S^{\mathrm{H}}{}_{\mathrm{trans}}(t) + S^{\mathrm{H_2}}{}_{\mathrm{trans}}(t) + S^{\mathrm{H_2}}{}_{\mathrm{rot}}(t) + S^{\mathrm{H_2}}{}_{\mathrm{vib}}(t) \quad (1)$$

Evaluation of the translational contributions to the entropy using the Sackur–Tetrode equation requires only a knowledge of the translational temperature, the volume and the number of particles of each kind, together with their respective masses. The number of He atoms is constant, and the numbers of H_2 molecules and H atoms are readily obtained from the distribution functions (*cf.* eq 6b); the instantaneous value of the temperature follows from energy conservation, the energy going into vibration and dissociation being calculated directly from the distribution function, and the rotational energy of the remaining H_2 molecules being considered as classical at these temperatures. The rotational entropy of the H_2 molecules was calculated from the mean rotational partition function, which itself was derived from the equilibrium constant K and the exact values of all the other partition functions occurring in the equilibrium-constant expression. The vibrational entropy of the H_2 molecules was assumed to be given under nonequilibrium conditions[16,17] by the expression

$$S_{\mathrm{vib}} = -k\sum_{i=0}^{n-1} p_i \ln p_i \quad (2)$$

where

$$p_i = n_i/\sum_{j=0}^{n-1} n_j \quad (3)$$

The evolution of the temperature and the individual entropy terms during the reaction is illustrated in Table IV, and in the last column the evolution of the total entropy of the system is shown as $[S(\infty) - S(t)]$. It can be seen that the entropy increases monotonically with time, as required by the H theorem.[19] Closer inspection reveals that this increase results mainly from the difference of two quite substantial terms, one an increase due to the increase in the number of particles and the other a decrease due to the cooling which accompanies dissociation; the overall increase is, however, guaranteed through the third law of thermodynamics.

In linear thermodynamics, it can be shown that $\mathrm{d}^2S/\mathrm{d}t^2$ is negative near equilibrium,[20] but its behavior in the nonlinear domain is not clear. Recently, however, it has been postulated by McKean[21] that successive $\mathrm{d}^nS/\mathrm{d}t^n$ alternate in sign; the truth of this postulate is now established for the linear domain, and for certain idealized models in the nonlinear domain.[22] We have taken our entropy data at 33 points between $t = 0$ and $t = \infty$, and carried out a series of numerical differentiations. We preset a limit of 20 successive differentiations (because we did not feel there would be much significance left in the numbers by then). The surprising result was that all 20 derivatives were alternately either positive throughout, or negative throughout, all the way from $t = 0$ to $t = \infty$! In fact, repeated differentiation appears to behave as a projection operator in the sense that the tenth derivative is strictly exponential[23] in the range $0 < t < 10^{-4}$ sec, and the 20th derivative is strictly exponential up to as far as 10^{-2} sec! Thus, McKean's postulate is established *for the master equation model of this system* in this time range, since further derivatives *must* now alternate in sign. In the remainder of the approach to equilibrium, it seems reasonable to infer that after 20 successful differentiations, the postulate could easily be valid *ad infinitum*.[24] Perhaps the fact that under certain conditions the solutions of Volterra integral equations are completely monotonic[25] is important here, despite the fact that there is a very indirect connection between $\xi(t)$ and $S(t)$.

4. Rate Constants. Table V presents some rate coefficients derived from the data in Tables II and III, as a function of the time t, and the percentage reaction. The third and fourth columns give the upward and downward fluxes respectively between the discrete and the continuum states, *i.e.*

$$R_{\mathrm{d}} = [\mathrm{M}]\sum_{i=0}^{n-1}\bar{W}_{ni}n_i \text{ and } R_{\mathrm{r}} = [\mathrm{M}]\sum_{i=0}^{n-1}\bar{W}_{in}n_n \quad (4)$$

These fluxes become equal, as expected, when $t \rightarrow \infty$. The fifth column contains the rate coefficient (r) for the upward flux calculated from the expression

$$R_{\mathrm{d}} = r[\mathrm{M}][\mathrm{H_2}] = r[\mathrm{M}]\sum_{i=0}^{n-1}n_i \quad (5)$$

The rate coefficient (r') for the downward flux is a constant, 8.361×10^{-35} cm^6 molecule^{-2} sec^{-1}; hence $r(\infty)/r' = K$; *cf.* ref 15. The sixth column of Table V gives the phenomenological rate constant k_{d} for the dissociation reaction derived from the phenomenological equation

$$\frac{-\mathrm{d}[\mathrm{H_2}]}{\mathrm{d}t} = k_{\mathrm{d}}[\mathrm{M}][\mathrm{H_2}] - k_{\mathrm{r}}[\mathrm{M}][\mathrm{H}]^2 \quad (6)$$

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(16) W. Yourgrau, A. van der Merwe, and G. Raw, "Treatise on Irreversible and Statistical Thermophysics," The Macmillan Co., New York, N. Y., 1966.

(17) We note in passing that elegant formulas can be written[18] for the vibrational contribution to $\mathrm{d}S/\mathrm{d}t$ and $\mathrm{d}^2S/\mathrm{d}t^2$ in terms of the W_{ij}, but they are very difficult to use because of catastrophic cancellation.

(18) O. K. Rice, "Statistical Mechanics, Thermodynamics and Kinetics," W. H. Freeman & Co., San Francisco, Calif., 1967.

(19) In a thermodynamic sense, therefore, at no time in the relaxation can one say that there is a "steady state," except when equilibrium is attained; a true "steady state" would only arise if the conservation condition were relaxed.

(20) T. A. Bak, "Contributions to the Theory of Chemical Kinetics," W. A. Benjamin, Inc., New York, N. Y., 1963.

(21) H. P. McKean, *Arch. Ratl. Mech. Anal.*, **21**, 343 (1966).

(22) S. Harris, *J. Math. Phys.*, **8**, 2407 (1967).

(23) It may easily be verified by examination of Table IV (which is a representative sample of the 33 points used) that the entropy function itself is not a pure exponential. We are a little wary of this projecting out of a pure exponential; it is conceivable that it could be a property of the differentiation algorithm (IBM Scientific Subroutine Package DDGT3; *cf.* F. B. Hilderbrand, "Introduction to Numerical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 64–68), given a suitable function whose first few derivatives alternate in sign.

(24) A little elaboration is appropriate here. Firstly, some care is necessary to eliminate "end effects" and also in avoiding overflow at small t, or underflow at large t. Secondly, after five differentiations, the "join" in the two solutions showed up as a step at 10^{-6} sec; the result described above was, therefore, only obtained by omitting points close to the join, and no points in the range $10^{-7} < t < 10^{-5}$ sec were actually included. One is reminded here of the physical chemist's "proof" that all odd numbers are prime numbers: 1 is a prime number; so are 3, and 5, and 7. Nine? Well that's experimental error. Eleven is a prime number; so is 13. Now we have done enough experiments to prove it!

(25) A. Friedman, *J. Anal. Math.*, **11**, 381 (1963).

Table II. Assumed Set of Probabilities (P_{ij}) per Collision for the Relaxation of H_2 by He at 2000°K[a,b]

	$v = 0$	$v = 1$	$v = 2$	$v = 3$	$v = 4$	$v = 5$	$v = 6$	$v = 7$
$v = 0$		3.7×10^{-4}	5.6×10^{-8}	2×10^{-12}	5×10^{-17}	1×10^{-20}	4×10^{-22}	1×10^{-22}
$v = 1$	7.3×10^{-3}		8.9×10^{-4}	2.7×10^{-7}	2×10^{-11}	7×10^{-16}	8×10^{-19}	2×10^{-20}
$v = 2$	1.9×10^{-5}	1.5×10^{-2}		1.7×10^{-3}	9.2×10^{-7}	9×10^{-11}	6×10^{-15}	3×10^{-18}
$v = 3$	9.1×10^{-9}	6.5×10^{-5}	2.5×10^{-2}		3.1×10^{-3}	2.6×10^{-6}	4×10^{-10}	4×10^{-14}
$v = 4$	3×10^{-12}	4.7×10^{-8}	1.6×10^{-4}	3.7×10^{-2}		5.1×10^{-3}	7.1×10^{-6}	1.5×10^{-9}
$v = 5$	9×10^{-15}	2×10^{-11}	1.6×10^{-7}	3.3×10^{-4}	5.3×10^{-2}		8.3×10^{-3}	1.9×10^{-5}
$v = 6$	2×10^{-15}	2×10^{-13}	9×10^{-11}	4.3×10^{-7}	6.4×10^{-4}	7.3×10^{-2}		1.3×10^{-2}
$v = 7$	5×10^{-15}	3×10^{-14}	3×10^{-13}	3×10^{-10}	1.0×10^{-6}	1.2×10^{-3}	9.7×10^{-2}	
$v = 8$	1×10^{-14}	4×10^{-14}	9×10^{-14}	2×10^{-12}	9×10^{-10}	2.4×10^{-6}	2.0×10^{-3}	1.3×10^{-1}
$v = 9$	2×10^{-15}	2×10^{-14}	4×10^{-14}	1×10^{-13}	1×10^{-11}	2.3×10^{-9}	4.8×10^{-6}	3.2×10^{-3}
$v = 10$	1×10^{-15}	2×10^{-15}	1×10^{-15}	1×10^{-14}	2×10^{-15}	3×10^{-11}	5.2×10^{-9}	8.8×10^{-6}
$v = 11$	8×10^{-17}	1×10^{-16}	5×10^{-16}	7×10^{-15}	5×10^{-14}	1×10^{-12}	4×10^{-11}	9.4×10^{-9}
$v = 12$	2×10^{-17}	1×10^{-15}	8×10^{-15}	1×10^{-14}	1×10^{-14}	2×10^{-15}	3×10^{-13}	5×10^{-11}
$v = 13$	8×10^{-17}	1×10^{-16}	4×10^{-17}	7×10^{-18}	4×10^{-17}	5×10^{-17}	1×10^{-14}	2×10^{-13}
$v = 14$	5×10^{-21}	1×10^{-19}	6×10^{-19}	1×10^{-18}	5×10^{-19}	4×10^{-19}	4×10^{-20}	9×10^{-17}
Pairs	9×10^{-31}	2×10^{-29}	9×10^{-29}	2×10^{-28}	9×10^{-29}	1×10^{-27}	7×10^{-27}	6×10^{-22}

[a] The elements W_{ij} of eq I(8), etc., are derived from these P_{ij} by forming the product $W_{ij} = ZP_{ij}$ where Z is a collision number between

which, if it can be assumed that the equilibrium constant for the reaction conforms to the rate-quotient law,[8,15,26,27] becomes

$$\frac{-\mathrm{d}[H_2]}{\mathrm{d}t} = k_d[M][H_2] - K^{-1}k_d[M][H]^2 \qquad (6a)$$

Recasting in terms of the quantities available in Tables II and III, eq 6a has the form

$$[M]\sum_{i=0}^{n-1}[\bar{W}_{in}n_n - \bar{W}_{ni}n_i] = k_d[M]\left\{\sum_{i=0}^{n-1} n_i - K^{-1}[2(n_n + n_{(n+1)})]^2\right\} \qquad (6b)$$

It can be seen that after the initial period, k_d remains constant to the number of figures given,[28] and that it is indistinguishable from r, as would be expected from a comparison of eq 4, 5, and 6b, so long as the back-reaction is unimportant. At later times, r is greater than k_d as was foreseen by Widom.[15]

However, the experimenter is not always in a position to use eq 6a in reducing his results. One common approach is to try to evaluate the "initial rate" by extrapolation of the rate data back to zero time; this should lead to an evaluation of $r \equiv k_d$ at these early times. Alternatively, many workers use the integrated form of the rate equation. Here one has two choices, either to work at low percentage conversions and use a first-order rate law, or to use the full integrated form of the rate equation. The first-order rate law, which ignores the back-reaction, is

$$\frac{-\mathrm{d}[H_2]}{\mathrm{d}t} = k_d[M][H_2] \qquad (7)$$

or in integral form

$$k_d^{F} = t^{-1}[M]^{-1} \ln \{a_0/a_t\} \qquad (8)$$

where $a_t \equiv [H_2]_t$. Comparison of the atom concentrations in Table IIIb or Table V for values of log $t = -5, -4, -3, -2$, and -1 is striking confirmation of the validity of (8) up to about 20% reaction. The full integrated rate law, derived from (6a), is

$$k_d^{I} = t^{-1}[M]^{-1}\gamma\{\tanh^{-1}[-\gamma] - \tanh^{-1}[-\gamma(1 + 4x_t/K)]\} \qquad (9)$$

where $x_t \equiv [H]_t$, K is the equilibrium constant, and $\gamma = \{1 + 16a_0/K\}^{-1/2}$; an equivalent expression in logarithmic form is also available.[29] The first-order intergrated rate constant k_d^F and the correct integrated rate constant k_d^I are more or less indistinguishable up to about 5% reaction.

5. Nearest Neighbor Transitions. It is quite clear from simple considerations[10] that nonnearest neighbor transitions dominate the transient period, but soon become quite unimportant as far as the vibrational part of the relaxation is concerned. On the other hand, it has been maintained[30] that observed dissociation rates for some diatomic molecules cannot be explained without invoking nonnearest neighbor transitions. The two following calculations throw considerable light on the problem. First, we explored a nearest-neighbor-only model, in which all probabilities W_{ij} in Table II were put equal to zero *except* these for $i = j \pm 1$; this involves a complete recalculation since the **A** matrix is changed through eq I(18). It was found that in the very early stages of the vibrational relaxation, the evolution was retarded by comparison with the figures in Table III(a); nevertheless, long before the chemical reaction had begun, say in the period 10^{-7}–10^{-5} sec, the population distribution arising from the nearest-neighbor-only model had become identical with that shown in Table III. However, at say 10^{-1} sec, the reaction had gone only to about 11% instead of the 21% shown in Table III(b); corresponding figures for 1 sec are 75% instead of 96%; thus with our W_{ij}, the reduction in rate is not as marked as suggested in ref 30. We then repeated the calculation with a restricted set of W_{ij} where only nearest neighbor transitions were allowed below $v = 10$, but all transitions were allowed above $v = 10$. The principal effect here is to allow the parallel dissociation paths, and it was found that although the evolution was

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(26) H. O. Pritchard, *J. Phys. Chem.*, **66**, 2111 (1962).

(27) O. K. Rice, *ibid.*, **65**, 1972 (1961); **67**, 1733 (1963).

(28) There is a small systematic change in k_d as the reaction progresses. This can be regarded as the result of the time dependence of one of the eigenvalues of the system; *cf.* Part I.[3] Alternatively, one could regard it as being the result of the fact that in writing $K^{-1}[H]^2$ in eq 6a, one is assuming that these atoms were derived from hydrogen molecules having their equilibrium chemical potential, whereas this is not quite the case; *cf.* Tables III and IV.

(29) Any table of integrals; see, *e.g.*, "Handbook of Chemistry and Physics," The Chemical Rubber Co., Cleveland, Ohio.

(30) W. G. Valance, E. W. Schlag, and J. P. Elwood, *J. Chem. Phys.*, **47**, 3284 (1967).

$v = 8$	$v = 9$	$v = 10$	$v = 11$	$v = 12$	$v = 13$	$v = 14$	Pairs
5×10^{-23}	1×10^{-24}	2×10^{-25}	4×10^{-27}	5×10^{-28}	8×10^{-28}	3×10^{-32}	5×10^{-39}
3×10^{-21}	3×10^{-22}	8×10^{-24}	1×10^{-25}	4×10^{-25}	3×10^{-26}	1×10^{-29}	2×10^{-36}
1×10^{-19}	1×10^{-20}	7×10^{-23}	8×10^{-24}	5×10^{-23}	1×10^{-25}	1×10^{-27}	2×10^{-34}
5×10^{-17}	5×10^{-19}	1×10^{-20}	2×10^{-21}	1×10^{-21}	3×10^{-25}	3×10^{-26}	4×10^{-33}
2×10^{-13}	5×10^{-16}	2×10^{-20}	1×10^{-19}	1×10^{-20}	2×10^{-23}	2×10^{-25}	3×10^{-32}
5.9×10^{-9}	1×10^{-12}	3×10^{-15}	4×10^{-17}	3×10^{-20}	3×10^{-22}	1×10^{-24}	4×10^{-30}
4.3×10^{-5}	2.0×10^{-8}	5×10^{-12}	1×10^{-14}	3×10^{-17}	5×10^{-19}	1×10^{-24}	2×10^{-28}
2.1×10^{-2}	1.0×10^{-4}	6.3×10^{-8}	2×10^{-11}	3×10^{-14}	6×10^{-17}	2×10^{-20}	1×10^{-22}
	3.1×10^{-2}	2.1×10^{-4}	1.8×10^{-7}	4×10^{-11}	4×10^{-14}	6×10^{-18}	9×10^{-19}
1.6×10^{-1}		4.4×10^{-2}	4.3×10^{-4}	2.7×10^{-7}	4×10^{-11}	4×10^{-15}	7×10^{-15}
4.8×10^{-3}	1.9×10^{-1}		6.3×10^{-2}	5.1×10^{-4}	2.6×10^{-7}	5×10^{-12}	6×10^{-11}
1.4×10^{-5}	6.4×10^{-3}	2.2×10^{-1}		5.8×10^{-2}	5.9×10^{-4}	9.1×10^{-8}	2.7×10^{-6}
8.0×10^{-9}	1.1×10^{-5}	4.9×10^{-3}	1.6×10^{-1}		4.1×10^{-2}	5.4×10^{-4}	5.9×10^{-3}
2×10^{-11}	3.5×10^{-9}	5.3×10^{-6}	3.5×10^{-3}	8.7×10^{-2}		2.2×10^{-2}	2.2×10^{-2}
4×10^{-15}	5×10^{-13}	2×10^{-10}	8.4×10^{-7}	1.8×10^{-3}	3.5×10^{-2}		4.6×10^{-2}
7×10^{-19}	1×10^{-15}	2×10^{-12}	2.5×10^{-8}	2.0×10^{-5}	3.5×10^{-5}	4.7×10^{-5}	

H_2 and He. [b] Upper half = activation; lower half = deactivation.

Table III(a). Evolution of the Population Distribution Function $\xi_i = n_i/\tilde{n}_i$ as a Function of Time at 2000°K, Calculated by Runge–Kutta Integration

	Log t					
State i	$-\infty$	-10	-9	-8	-7	-6
$v = 0$	1.062039	1.060078	1.045477	1.009843	1.008320	1.008320
$v = 1$	0.0	3.90×10^{-2}	0.324448	0.981438	1.008320	1.008320
$v = 2$	0.0	1.57×10^{-3}	0.103135	0.954830	1.008320	1.008320
$v = 3$	0.0	7.43×10^{-5}	3.55×10^{-2}	0.932349	1.008320	1.008320
$v = 4$	0.0	4.05×10^{-6}	1.32×10^{-2}	0.913381	1.008319	1.008319
$v = 5$	0.0	2.62×10^{-7}	5.39×10^{-3}	0.897887	1.008316	1.008316
$v = 6$	0.0	1.99×10^{-8}	2.40×10^{-3}	0.885184	1.008295	1.008295
$v = 7$	0.0	1.78×10^{-9}	1.15×10^{-3}	0.874535	1.008177	1.008177
$v = 8$	0.0	1.9×10^{-10}	6.08×10^{-4}	0.865454	1.007635	1.007635
$v = 9$	0.0	2.2×10^{-11}	3.34×10^{-4}	0.855908	1.005374	1.005374
$v = 10$	0.0	2.8×10^{-12}	1.89×10^{-4}	0.842240	0.997298	0.997298
$v = 11$	0.0	3.9×10^{-13}	1.10×10^{-4}	0.816009	0.973116	0.973116
$v = 12$	0.0	3.8×10^{-14}	5.34×10^{-5}	0.732204	0.880944	0.880944
$v = 13$	0.0	2.7×10^{-15}	1.71×10^{-5}	0.526852	0.641557	0.641557
$v = 14$	0.0	1.0×10^{-16}	2.66×10^{-6}	0.233981	0.289881	0.289881
Pairs	0.0	0.0	5.5×10^{-29}	3.3×10^{-17}	2.7×10^{-14}	3.1×10^{-12}
Atoms	0.0	0.0	7.4×10^{-15}	5.74×10^{-9}	1.65×10^{-7}	1.76×10^{-6}

again retarded for the first 10^{-9} sec, for the remainder of the relaxation, the results were indistinguishable from those in Table III. Thus, we conclude that in future calculations, a judicious blend of nearest neighbor and nonnearest neighbor transitions could be used, particularly at low temperatures where the vibrational and chemical parts of the relaxation are not strongly coupled. While this would give some economy in the solution of the master equation itself, the principal effect would be to eliminate the need for calculating transition probabilities of multiple quantum jumps involving low-lying states as a prerequisite to such a solution.

B. Recombination

1. The Model. The hypothetical experiment simulated here is the reverse of that described above. It is imagined that a mixture consisting of 3.5×10^{16} molecules/cc of H_2 diluted in 3.5×10^{19} atoms/cc of He has been subjected to some process which instantaneously dissociates all the H_2 molecules into ground-state H atoms. This instant is taken to be $t = 0$, and the translational temperature T_0' is chosen so that when equilibrium is eventually attained, the final temperature will be 2000°K. Again, the process takes place at constant volume and at constant energy, and translational–rotational equilibration is assumed to be very rapid; thus, each newly formed H_2 molecule automatically contributes to the rotational energy and rotational entropy to an extent characteristic of the instantaneous translational temperature of the system.

2. The Relaxation. The method of solution used was identical with that used for the dissociation calculation, *i.e.*, Runge–Kutta integration out to 10^{-6} sec followed by the iterative application of eq I(29a) at intervals of $\Delta \log t = 0.2$. The initial distribution $\xi(0)$ was taken to consist only of atoms, together with the appropriate number of pairs specified by eq I(3), and the evolution of $\xi(t)$, using the transition probabilities of Table II, is shown in Table VI. The changes in population are rather more complicated than in the dissociation case, and Table VI is divided into three sections: VI(a) shows the very early stages of the recombination; VI(b), the main body of the reaction; and VI(c), the final approach to equilibrium.

One of the principal features of the relaxation is the appearance of a relatively well-defined bottleneck effect, although the actual position of the change from over to under population does not appear to be quite constant. Above this bottleneck, the levels are always grossly overpopulated, and not really in equilibrium with each other[26] except in the very final stages of the reaction. The lower levels are, of course, grossly underpopulated

Table III(b). Evolution of the Population Distribution Function $\xi_i = n_i/\bar{n}_i$ as a Function of Time at 2000°K, Calculated by the Iterative Application of Eq I(29a)

State i	Log t												
	−5	−4	−3	−2	−1.4	−1	−0.8	−0.6	−0.4	−0.2	0	0.2	0.4
$v = 0$	1.008320	1.008318	1.008302	1.008138	1.007599	1.006538	1.005571	1.004223	1.002615	1.001165	1.000313	1.000039	1.000001
$v = 1$	1.008320	1.008318	1.008302	1.008138	1.007599	1.006538	1.005571	1.004223	1.002615	1.001165	1.000313	1.000039	1.000001
$v = 2$	1.008320	1.008318	1.008302	1.008138	1.007599	1.006538	1.005571	1.004223	1.002615	1.001165	1.000313	1.000039	1.000001
$v = 3$	1.008320	1.008318	1.008302	1.008138	1.007599	1.006538	1.005571	1.004223	1.002615	1.001165	1.000313	1.000039	1.000001
$v = 4$	1.008319	1.008318	1.008301	1.008138	1.007599	1.006538	1.005570	1.004223	1.002615	1.001165	1.000313	1.000039	1.000001
$v = 5$	1.008316	1.008314	1.008298	1.008134	1.007595	1.006534	1.005567	1.004220	1.002613	1.001164	1.000313	1.000039	1.000001
$v = 6$	1.008294	1.008293	1.008277	1.008113	1.007574	1.006514	1.005548	1.004204	1.002602	1.001158	1.000311	1.000038	1.000001
$v = 7$	1.008177	1.008175	1.008159	1.007996	1.007458	1.006402	1.005444	1.004115	1.002540	1.001128	1.000303	1.000037	1.000001
$v = 8$	1.007635	1.007634	1.007617	1.007454	1.006920	1.005886	1.004962	1.003706	1.002254	1.000987	1.000263	1.000032	1.000001
$v = 9$	1.005373	1.005372	1.005356	1.005194	1.004677	1.003731	1.002951	1.001997	1.001059	1.000400	1.000096	1.000011	1.000000
$v = 10$	0.997298	0.997296	0.997280	0.997124	0.996667	0.996037	0.995772	0.995896	0.996794	0.998305	0.999501	0.999936	0.999997
$v = 11$	0.973116	0.973114	0.973099	0.972957	0.972682	0.972997	0.974274	0.977627	0.984023	0.992029	0.997720	0.999709	0.999989
$v = 12$	0.880944	0.880943	0.880929	0.880846	0.881262	0.885180	0.892334	0.907992	0.935345	0.968109	0.990930	0.998847	0.999956
$v = 13$	0.641557	0.641556	0.641547	0.641615	0.643827	0.657103	0.679518	0.727138	0.808919	0.905986	0.973296	0.996609	0.999873
$v = 14$	0.289881	0.289881	0.289880	0.290168	0.295019	0.322042	0.366878	0.461452	0.623191	0.814721	0.947391	0.993320	0.999750
Pairs	4.7×10^{-10}	4.75×10^{-8}	4.76×10^{-6}	4.76×10^{-4}	0.007500	0.045855	0.109173	0.242449	0.470097	0.739494	0.926038	0.990609	0.999648
Atoms	2.15×10^{-5}	2.18×10^{-4}	0.002182	0.021821	0.086608	0.214139	0.330413	0.492391	0.685636	0.859938	0.962308	0.995293	0.999824

at the beginning of the relaxation, and it is not until about 10^{-4} sec that any semblance of equilibrium appears among a series of neighboring levels; as time progresses, however, more and more of the lower levels come into equilibrium with each other. The upper levels (after their initial buildup) approach their equilibrium populations monotonically from above, and the lower levels approach from below, just the converse of the dissociation case; however, there are a few levels in the middle, in the bottleneck region, which are subject to minor population alternation.

3. Entropies. The behavior of the total entropy associated with the relaxation described in Table VI is shown in Table VII, calculated using eq 1–3. It is immediately clear that in the recombination both the temperature and entropy changes are much larger than they were in the dissociation (if both processes take place at around 2000°K). In the recombination process, the loss in entropy due to the reduction in the total number of particles is more than offset by the accompanying increase in temperature, and the total entropy rises monotonically with time, as it must. In fact, the results again support McKean's complete monotonicity hypothesis[21] to the extent that the first 20 time derivatives of the entropy are alternately either positive throughout, or negative throughout.[31]

It might be argued that this is surprising because of the approximation embodied in eq I(22a), *i.e.*, that the transition probabilities W_{ij} do not change during the process. Even if the probabilities for deactivation were assumed to remain unchanged, we should really readjust the activation probabilities to obey detailed balancing at the current value of the translational temperature. However, it can readily be seen [*e.g.*, eq I(8)] that [M] and t are conjugate quantities. Hence, the population distribution functions $\xi(t)$ of Tables VI and III would be equally appropriate to a scaled value of t if [M] were different, and it is quite easy to imagine an increase in the inert-gas concentration sufficient to make the approximation I(22a) reasonably acceptable. To a large extent, the same is true of the entropies in Tables VII and IV, but the scaling here is not quite linear, and it therefore seems slightly fortuitous that the entropy and all its derivatives turn out to be so well behaved.

4. Rate Constants. Table VIII presents some rate coefficients derived from the data in Tables VI and II as a function of the time t. Column two of this table gives $\xi_0(t)$ as a measure of the extent of reaction, and the third and fourth columns give the upward and downward fluxes, respectively, calculated according to eq 4. They become equal, of course, as $t \rightarrow \infty$, but their most interesting feature is that they never differ by more than a factor of about 2 once the initial transient period is completed. Moreover, in the early stages of the relaxation, these fluxes are enormous. As a consequence of this, while the rate coefficient (r') for the downward flux, calculated from

$$R_r = r'[\mathrm{M}][\mathrm{H}]^2 \qquad (10)$$

remains constant at 8.361×10^{-35} cm^6 molecule^{-2} sec^{-1},

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(31) Unlike the dissociation case, probably because the entropy changes are larger, the "join" in the solutions at 10^{-6} sec did not show up in these differentiations; consequently, it was not necessary to omit any of the 39 points to obtain this result. Like the dissociation case, however, we also observed the same curious projecting-out phenomenon.

Table IV. Temperature and Entropy as a Function of Time in the Dissociation of Hydrogen at 2000°K[a]

		$S_{\text{trans}}(t)$			H_2		
Log *t*	*T*, °K	He	H	H_2	$S_{\text{rot}}(t)$	$S_{\text{vib}}(t)$	$[S(\infty) - S(t)]$
$-\infty$	2000.5030	85,343.3402	0.0	113.7497	16.9787	0.0	0.33094
−10	2000.4956	85,343.3135	0.0000	113.7496	16.9787	0.0652	0.29248
−9	2000.4397	85,343.1109	0.0000	113.7494	16.9785	0.3955	0.16509
−8	2000.2955	85,342.5887	0.0000	113.7489	16.9782	1.0037	0.08809
−7	2000.2891	85,342.5655	0.0000	113.7489	16.9782	1.0270	0.07998
−6	2000.2891	85,342.5655	0.0000	113.7489	16.9782	1.0270	0.07998
−5	2000.2891	85,342.5654	0.0001	113.7489	16.9782	1.0270	0.07996
−4	2000.2891	85,342.5652	0.0006	113.7487	16.9781	1.0270	0.07982
−3	2000.2885	85,342.5632	0.0058	113.7469	16.9779	1.0270	0.07874
−2	2000.2828	85,342.5426	0.0542	113.7292	16.9751	1.0268	0.07157
−1.4	2000.2641	85,342.4747	0.2054	113.6710	16.9660	1.0263	0.05614
−1	2000.2272	85,342.3411	0.4925	113.5562	16.9480	1.0252	0.03650
−0.8	2000.1936	85,342.2193	0.7484	113.4516	16.9317	1.0242	0.02432
−0.6	2000.1468	85,342.0496	1.0997	113.3058	16.9088	1.0228	0.01272
−0.4	2000.0909	85,341.8472	1.5132	113.1319	16.8816	1.0212	0.00445
−0.2	2000.0405	85,341.6645	1.8823	112.9750	16.8571	1.0197	8.26×10^{-4}
0	2000.0109	85,341.5573	2.0978	112.8829	16.8427	1.0189	5.77×10^{-5}
0.2	2000.0014	85,341.5227	2.1670	112.8532	16.8380	1.0186	8.90×10^{-7}
0.4	2000.0001	85,341.5180	2.1765	112.8491	16.8374	1.0185	1.24×10^{-9}
0.6	2000.0000	85,341.5178	2.1769	112.8489	16.8374	1.0185	1.45×10^{-11}

[a] Entropies are in units of ergs deg^{-1} cm^{-3}.

Table V. Variation with Time of the Upward and Downward Fluxes, the Rate Coefficient, and the Phenomenological Rate Constant for the Dissociation of Hydrogen at 2000°K

Log *t*	% reaction	$10^{-14}R_d$[a]	$10^{-14}R_r$[a]	$10^{22}r$[b]	$10^{22}k_d$[b]
−10	...	8×10^{-14}	...	6.8×10^{-14}	6.8×10^{-14}
−9	7.4×10^{-13}	1.7×10^{-4}	5×10^{-28}	1.4×10^{-4}	1.4×10^{-4}
−8	5.7×10^{-7}	4.220	3×10^{-15}	3.445	3.445
−7	1.65×10^{-5}	5.140	2×10^{-13}	4.196	4.196
−6	1.76×10^{-4}	5.140	3×10^{-11}	4.196	4.196
−5	2.15×10^{-3}	5.140	4.5×10^{-9}	4.196	4.196
−4	2.18×10^{-2}	5.140	4.6×10^{-7}	4.196	4.196
−3	2.18×10^{-1}	5.140	4.6×10^{-5}	4.196	4.196
−2	2.18	5.142	4.6×10^{-3}	4.198	4.196
−1.4	8.66	5.172	7.3×10^{-2}	4.225	4.196
−1	21.4	5.345	4.4×10^{-1}	4.371	4.196
−0.8	33.0	5.636	1.065	4.613	4.196
−0.6	49.2	6.250	2.367	5.123	4.196
−0.4	68.5	7.304	4.589	5.996	4.196
−0.2	85.9	8.553	7.219	7.032	4.196
0	96.2	9.419	9.040	7.751	4.196
0.2	99.5	9.719	9.671	7.999	4.196
0.4	99.98	9.761	9.759	8.034	4.196
0.6	99.9999	9.763	9.763	8.036	4.196

[a] Units of molecules cm^{-3} sec^{-1}. [b] Units of cm^{3} molecule^{-1} sec^{-1}.

Table VI(a). Evolution of the Population Distribution Function $\xi_i = n_i/\bar{n}_i$ as a Function of Time at 2000°K, Calculated by Runge–Kutta Integration[a]

	Log *t*					
State *i*	$-\infty$	−10	−9	−8	−7	−6
$v = 0$	0.0	3.8×10^{-23}	7.78×10^{-13}	6.96×10^{-7}	1.99×10^{-5}	2.14×10^{-4}
$v = 1$	0.0	1.4×10^{-19}	3.73×10^{-10}	1.00×10^{-5}	3.13×10^{-5}	2.25×10^{-4}
$v = 2$	0.0	2.3×10^{-16}	6.75×10^{-8}	1.05×10^{-4}	1.29×10^{-4}	3.23×10^{-4}
$v = 3$	0.0	1.9×10^{-13}	5.66×10^{-6}	9.43×10^{-4}	9.71×10^{-4}	1.16×10^{-3}
$v = 4$	0.0	8.2×10^{-11}	2.51×10^{-4}	7.81×10^{-3}	7.84×10^{-3}	8.03×10^{-3}
$v = 5$	0.0	1.97×10^{-8}	6.20×10^{-3}	5.69×10^{-2}	5.70×10^{-2}	5.71×10^{-2}
$v = 6$	0.0	2.64×10^{-6}	9.20×10^{-2}	3.66×10^{-1}	3.66×10^{-1}	3.67×10^{-1}
$v = 7$	0.0	2.07×10^{-4}	8.95×10^{-1}	2.07	2.07	2.07
$v = 8$	0.0	9.23×10^{-3}	5.97	9.96	9.96	9.96
$v = 9$	0.0	2.48×10^{-1}	3.13×10	4.29×10	4.29×10	4.28×10
$v = 10$	0.0	4.11	1.31×10^{2}	1.60×10^{2}	1.60×10^{2}	1.60×10^{2}
$v = 11$	0.0	4.19×10	4.51×10^{2}	5.12×10^{2}	5.12×10^{2}	5.12×10^{2}
$v = 12$	0.0	3.96×10^{2}	1.72×10^{3}	1.85×10^{3}	1.85×10^{3}	1.85×10^{2}
$v = 13$	0.0	1.41×10^{3}	5.06×10^{3}	5.34×10^{3}	5.34×10^{3}	5.33×10^{3}
$v = 14$	0.0	2.95×10^{3}	1.00×10^{4}	1.04×10^{4}	1.04×10^{4}	1.04×10^{4}
Pairs	1.46×10^{4}	1.46×10^{4}	1.46×10^{4}	1.46×10^{4}	1.46×10^{4}	1.46×10^{4}
Atoms	1.21×10^{2}	1.21×10^{2}	1.21×10^{2}	1.21×10^{2}	1.21×10^{2}	1.21×10^{2}

[a] As was the case in the dissociation reaction, Table III, some of these values of ξ_i at very early times represent less than one molecule: these should be interpreted in the light of our comment in paper I that the master equation formulation implies that time and therefore the concentrations are continuous variables.

Table VI(b). Evolution of the Population Distribution Function $\xi_i = n_i/\bar{n}_i$ as a Function of Time at 2000°K, Calculated by the Iterative Application of Eq I(29a)

State i	Log t											
	−5	−4	−3.2	−3	−2.8	−2.6	−2.4	−2.2	−2	−1.8	−1.4	−1
$v = 0$	0.002150	0.021113	0.119702	0.177076	0.253697	0.348809	0.456917	0.568514	0.673225	0.763309	0.889494	0.955372
$v = 1$	0.002161	0.021124	0.119711	0.177084	0.253703	0.348814	0.456921	0.568516	0.673226	0.763309	0.889494	0.955372
$v = 2$	0.00225	0.02121	0.11978	0.17715	0.25375	0.34885	0.45695	0.568535	0.673237	0.763315	0.889495	0.955372
$v = 3$	0.00309	0.02202	0.1204	0.1777	0.2542	0.3492	0.4572	0.56869	0.67333	0.76336	0.889507	0.955374
$v = 4$	0.00994	0.0286	0.1257	0.1823	0.2580	0.3521	0.4592	0.5700	0.6740	0.76377	0.88960	0.95539
$v = 5$	0.0589	0.0757	0.163	0.215	0.285	0.373	0.473	0.5793	0.6795	0.7666	0.8902	0.95552
$v = 6$	0.367	0.372	0.404	0.426	0.459	0.505	0.566	0.638	0.713	0.784	0.8945	0.9563
$v = 7$	2.07	2.01	1.73	1.59	1.41	1.23	1.07	0.964	0.902	0.886	0.918	0.9609
$v = 8$	9.92	9.57	7.86	6.95	5.83	4.61	3.43	2.46	1.77	1.35	1.02	0.982
$v = 9$	4.27×10	4.11×10	3.34×10	2.93×10	2.42×10	1.87×10	1.32×10	8.73	5.41	3.29	1.48	1.07
$v = 10$	1.59×10^2	1.53×10^2	1.24×10^2	1.09×10^2	9.01×10	6.90×10	4.84×10	3.11×10	1.83×10	1.02×10	3.10	1.38
$v = 11$	5.10×10^2	4.91×10^2	3.98×10^2	3.48×10^2	2.87×10^2	2.19×10^2	1.53×10^2	9.80×10	5.72×10	3.10×10	7.97	2.33
$v = 12$	1.84×10^3	1.77×10^3	1.44×10^3	1.26×10^3	1.03×10^3	7.93×10^2	5.55×10^2	3.53×10^2	2.05×10^2	1.10×10^2	2.65×10	5.95
$v = 13$	5.31×10^3	5.11×10^3	4.14×10^3	3.63×10^3	2.99×10^3	2.28×10^3	1.59×10^3	1.01×10^3	5.90×10^2	3.15×10^2	7.47×10	1.53×10
$v = 14$	1.04×10^4	1.00×10^4	8.12×10^3	7.11×10^3	5.86×10^3	4.47×10^3	3.12×10^3	1.99×10^3	1.15×10^3	6.18×10^2	1.45×10^2	2.91×10
Pairs	1.46×10^4	1.40×10^4	1.14×10^4	9.97×10^3	8.22×10^3	6.28×10^3	4.39×10^3	2.79×10^3	1.62×10^3	8.67×10^2	2.03×10^2	4.04×10
Atoms	1.20×10^2	1.18×10^2	1.06×10^2	9.98×10	9.06×10	7.92×10	6.62×10	5.28×10	4.02×10	2.94×10	1.42×10	6.36

the rate coefficient (r) for the upward flux decreases by 11 orders of magnitude during the relaxation.

The fifth column of Table VIII lists the phenomenological rate constant k_r for the recombination process, derived from the expression

$$\frac{d[H_2]}{dt} = k_r[M][H]^2 - k_d[M][H_2] \qquad (11)$$

$$= k_r[M][H]^2 - k_rK[M][H_2] \qquad (11a)$$

invoking the rate-quotient law. Equation 11a can now be recast in terms of the quantities available in Tables VI and II to give

$$[M]\sum_{i=0}^{n-1}[\bar{W}_{in}n_n - \bar{W}_{ni}n_i] =$$

$$k_r[M]\left\{[2(n_n + n_{(n+1)})]^2 - K\sum_{i=0}^{n-1} n_i\right\} \qquad (11b)$$

and it is found that, except during the transient period, k_r remains constant throughout the process.[32]

In experimental studies of recombination processes, it is again common[33] to use the integrated form of the rate-constant expression. If one neglects the existence of the redissociation reaction, this is simply the second-order rate law

$$k_r^S = t^{-1}[M]^{-1}\{x_t^{-1} - x_0^{-1}\} \qquad (12)$$

The correct integrated rate constant is

$$k_r^I = t^{-1}[M]^{-1}\gamma\{\tanh^{-1}[\gamma(2x_0 + {}^1/_2K)] - \tanh^{-1}[\gamma(2x_t + {}^1/_2K)]\} \qquad (13)$$

where K is the equilibrium constant and

$$\gamma = \{K({}^1/_4K + 2x_0)\}^{-1/2}$$

In both (12) and (13), $x_t \equiv [H]_t$. The two integrated rate constants are more-or-less indistinguishable up to about 0.1 sec, or say 95% of the atoms recombined; this is a consequence of the fact that at 2000°K the equilibrium mixture contains relatively few atoms.

There is, however, considerable difficulty in being sure what one is actually measuring in a recombination experiment.[26] Perusal of Tables VI(a) and VI(b) in the context of say the iodine-atom recombination experiment[33] will reveal the kind of ambiguities which could arise. We have investigated a number of conceivable fallacious "experiments" but have not found any case where the observed rate constant would differ appreciably from the correct value. However, we have pre-

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(32) There is, in fact, a small time dependence of k_r, which just shows up in Table VIII. This, however, is not due to the time dependence of the eigenvalues, which is a much smaller order effect, but is an artifact of the model. Equations 11 and 11b are not consistent with each other because of the appearance of the term n_n in the latter. Equation 11b is consistent with our model in which we have a preliminary equilibrium between atoms and pairs, but it is only consistent with eq 11 and a constant k_r if the local conservation condition $2(n_n + n_{(n+1)}) = [H]$ is relaxed to $2n_{(n+1)} = [H]$. The idea of pairs was introduced originally[8,10] as an aid to calculating transition probabilities between the continuum and the discrete states, and they are also instructive in understanding the gross over-populations of the topmost levels in the recombination. However, they are unnecessary in the formulation of the relaxation equations, and we intend to reformulate our method without them in the future. It is, nevertheless, a moot point as to whether the true phenomenological equation is (11) above, or whether it should include the effect of a preassociation before deactivation.

(33) K. E. Russell and J. Simons, *Proc. Roy. Soc.* (London), A217, 271(1953).

Table VI(c). Evolution of the Population Distribution Function $\xi_i = n_i/\bar{n}_i$ as a Function of Time at 2000°K, Calculated by the Iterative Application of Eq I(29a)

	Log t						
State i	−0.8	−0.6	−0.4	−0.2	0	0.2	0.4
$v = 0$	0.973479	0.985303	0.992739	0.997088	0.999219	0.999900	0.999996
$v = 1$	0.973479	0.985303	0.992739	0.997088	0.999219	0.999900	0.999996
$v = 2$	0.973479	0.985303	0.992739	0.997088	0.999219	0.999900	0.999996
$v = 3$	0.973480	0.985303	0.992739	0.997088	0.999219	0.999900	0.999996
$v = 4$	0.973488	0.985306	0.992740	0.997088	0.999219	0.999900	0.999996
$v = 5$	0.973543	0.985329	0.992748	0.997091	0.999219	0.999900	0.999996
$v = 6$	0.973893	0.985469	0.992801	0.997109	0.999224	0.999900	0.999996
$v = 7$	0.975825	0.986247	0.993095	0.997205	0.999247	0.999903	0.999996
$v = 8$	0.984721	0.989829	0.994445	0.997648	0.999353	0.999916	0.999996
$v = 9$	1.021869	1.004785	1.000085	0.999499	0.999795	0.999971	0.999998
$v = 10$	1.154500	1.058183	1.020220	1.006108	1.001375	1.000164	1.000006
$v = 11$	1.551672	1.218087	1.080516	1.025899	1.006107	1.000745	1.000027
$v = 12$	3.065512	1.827569	1.310337	1.101333	1.024143	1.002957	1.000110
$v = 13$	6.997228	3.410504	1.907224	1.297249	1.070984	1.008702	1.000324
$v = 14$	12.773192	5.735946	2.784093	1.585062	1.139798	1.017142	1.000639
Pairs	17.534244	7.652778	3.506884	1.822304	1.196521	1.024100	1.000899
Atoms	4.187391	2.766365	1.872667	1.349927	1.093856	1.011978	1.000449

Table VII. Temperature and Entropy as a Function of Time in the Recombination of Hydrogen Atoms at 2000°K[a]

		$S_{\text{trans}}(t)$			H_2		
Log t	T, °K	He	H	H_2	$S_{\text{rot}}(t)$	$S_{\text{vib}}(t)$	$[S(\infty) - S(t)]$
$-\infty$	1964.8391	85,212.9652	217.1910	0.0	0.0	0.0	44.2433
−9	1964.8391	85,212.9653	217.1910	0.0001	0.0000	0.0000	44.2432
−8	1964.8392	85,212.9656	217.1906	0.0004	0.0000	0.0000	44.2429
−7	1964.8399	85,212.9681	217.1866	0.0035	0.0004	0.0001	44.2409
−6	1964.8467	85,212.9932	217.1467	0.0330	0.0036	0.0003	44.2226
−5	1964.9148	85,213.2443	216.7486	0.3059	0.0361	0.0022	44.0623
−4	1965.5813	85,215.7025	212.8484	2.7705	0.3538	0.0216	42.7027
−3.2	1969.0468	85,228.4697	192.5105	14.7127	2.0066	0.1220	36.5781
−3	1971.0636	85,235.8896	180.6250	21.4334	2.9692	0.1804	33.3019
−2.8	1973.7572	85,245.7872	164.6899	30.2730	4.2556	0.2584	29.1354
−2.6	1977.1010	85,258.0555	144.8000	41.0945	5.8538	0.3553	24.2403
−2.4	1980.9019	85,271.9758	122.0255	53.2462	7.6723	0.4654	19.0142
−2.2	1984.8257	85,286.3183	98.2949	65.6636	9.5515	0.5791	13.9920
−2	1988.5078	85,299.7511	75.7746	77.2214	11.3168	0.6857	9.6499
−1.8	1991.6756	85,311.2883	56.1450	87.1037	12.8369	0.7775	6.2482
−1.4	1996.1134	85,327.4194	28.0573	100.8651	14.9685	0.9060	2.1832
−1	1998.4303	85,335.8273	12.9132	108.0163	16.0824	0.9731	0.5871
−0.8	1999.0672	85,338.1367	8.6370	109.9783	16.3887	0.9915	0.2673
−0.6	1999.4831	85,339.6443	5.7975	111.2585	16.5887	1.0036	0.1070
−0.4	1999.7446	85,340.5923	3.9828	112.0633	16.7145	1.0111	0.0355
−0.2	1999.8976	85,341.1467	2.9063	112.5339	16.7881	1.0156	8.91×10^{-3}
0	1999.9725	85,341.4183	2.3734	112.7644	16.8242	1.0177	1.54×10^{-3}
0.2	1999.9965	85,341.5051	2.2020	112.8381	16.8357	1.0184	1.59×10^{-4}
0.4	1999.9999	85,341.5173	2.1778	112.8485	16.8373	1.0185	5.77×10^{-6}
0.6	2000.0000	85,341.5178	2.1769	112.8489	16.8374	1.0185	3.15×10^{-8}

[a] Entropies are in units of ergs deg^{-1} cm^{-3}.

sented sufficient numerical information in this paper for other model fallacious experiments to be investigated.

5. Selective Population Experiments. It is possible to imagine a slight variation of the hypothetical recombination experiment described in this paper, where instead of an instantaneous dissociation, all the molecules are simultaneously loaded into one particular vibrational level. Thus, at $t = 0$, $\xi(0)$ consists only of one nonzero element, corresponding to the particular value of v. If v is above the bottleneck, say $v = 12$ or 13, it is found that after about 10^{-5} sec $\xi(t)$ looks like the population distribution for this value of t shown in Table VI(b). This is clearly consistent with the very high values of R_d and R_r exhibited in Table VIII. On the other hand, if v is below the bottleneck, say $v = 3$ or 4, the distribution after 10^{-5} sec is indistinguishable from that in Table III, because of the very rapid equilibration that takes place among the lower vibrational levels. However, if v is chosen to be near the bottleneck, a rapid equilibration is possible in both directions, and in our particular model, starting with all molecules in $v = 10$, it is found that after 10^{-5} sec, the system looks like a dissociation that has been in progress for about 10^{-2} sec. Thus, if and when such experiments become possible, there is a chance that anomalously fast relaxation rates may be found for some individual levels.

C. The Rate-Quotient Law

It is readily established from the values of k_d and k_r to be found in Tables V and VIII that once the initial transient is over (somewhere between 10^{-8} and 10^{-7} sec in this reaction at this temperature), the rate-quotient law is obeyed to the number of figures given. There are, as we have noted above, relatively insignificant time dependences in both rate constants, but these are

Table VIII. Variation of the Upward and Downward Fluxes, and of the Phenomenological Rate Constant for the Recombination of Hydrogen Atoms at 2000°K

Log t	$100\xi_0(t)$	R_d[a]	R_r[a]	$10^{35}k_r$[b]
−10	3.8×10^{-21}	1.880×10^{18}	1.433×10^{19}	7.262
−9	7.8×10^{-11}	6.541×10^{18}	1.433×10^{19}	4.544
−8	6.96×10^{-5}	6.849×10^{18}	1.433×10^{19}	4.365
−7	1.99×10^{-3}	6.849×10^{18}	1.433×10^{19}	4.365
−6	2.14×10^{-2}	6.846×10^{18}	1.433×10^{19}	4.365
−5	2.15×10^{-1}	6.820×10^{18}	1.427×10^{19}	4.365
−4	2.11	6.565×10^{18}	1.374×10^{19}	4.365
−3.2	11.9	5.319×10^{18}	1.113×10^{19}	4.365
−3	17.7	4.655×10^{18}	9.743×10^{18}	4.365
−2.8	25.3	3.836×10^{18}	8.029×10^{18}	4.365
−2.6	34.8	2.930×10^{18}	6.133×10^{18}	4.366
−2.4	45.6	2.048×10^{18}	4.287×10^{18}	4.366
−2.2	56.8	1.303×10^{18}	2.727×10^{18}	4.366
−2	67.3	7.569×10^{17}	1.583×10^{18}	4.366
−1.8	76.3	4.048×10^{17}	8.465×10^{17}	4.366
−1.4	88.9	9.599×10^{16}	1.991×10^{17}	4.366
−1	95.5	1.937×10^{16}	3.953×10^{16}	4.366
−0.8	97.3	8.675×10^{15}	1.711×10^{16}	4.366
−0.6	98.5	4.072×10^{15}	7.471×10^{15}	4.366
−0.4	99.2	2.141×10^{15}	3.423×10^{15}	4.366
−0.2	99.7	1.358×10^{15}	1.779×10^{15}	4.366
0	99.9	1.067×10^{15}	1.168×10^{15}	4.366
0.2	99.99	9.874×10^{14}	9.998×10^{14}	4.366
0.4	99.9996	9.767×10^{14}	9.771×10^{14}	4.366
0.6	100	9.763×10^{14}	9.763×10^{14}	4.366

[a] Units of molecules cm^{-3} sec^{-1}. [b] Units of cm^6 $molecule^{-2}$ sec^{-1}.

far too small to yield a detectable difference between the rate constant ratio k_d/k_r and the equilibrium constant K.

It can also be readily established by the application of eq 8 and 12 that the population distributions of Tables III and VI do not in general yield integrated rate constants equal to the values listed in the final columns of Tables V and VIII, respectively. Once one has a series of parallel processes, there is no need for the integrated form of the rate constant to equal the differential form. This may most easily be understood if we restrict ourselves to the consideration of a dissociation reaction in the region where eq 7 is valid. In detail, (7) becomes

$$[\mathrm{M}] \sum_{i=0}^{n-1} W_{ni}n_i = k[\mathrm{M}] \sum_{i=0}^{n-1} n_i \tag{7a}$$

and in order to integrate this into (8), it is implicit that the summation on the left-hand side is separable. But

$$\sum_{i=0}^{n-1} \bar{W}_{ni}n_i \leq \left(\sum_{i=0}^{n-1} \bar{W}_{ni}\right)\left(\sum_{i=0}^{n-1} n_i\right) \tag{7b}$$

is a well-known inequality,[34] and so, in general, the integration cannot be performed. We are indebted to one of the referees (Professor O. K. Rice) for pointing out, however, that once the transient period is over (*i.e.*, from 10^{-7} sec onwards) the n_i's remain very closely proportional to each other, and so the integration is possible on the basis of the figures presented in Table III. Hence, although the integrated and differential forms of k_d (and k_r) do, and should, differ wildly during the transient period, they ought to approach one another as time progresses. This has caused us to reexamine our convergence criteria, and we have concluded that the integration step $\Delta \log t = 0.2$ is too coarse. Reduction of the step length to $\Delta \log t = 0.02$ causes a very small adjustment of the populations given in Table III: the values of k_d remain unaffected, but k_d^{I} behaves more acceptably, differing from k_d by 10% at 10^{-7} sec but becoming indistinguishable from it beyond 10^{-5} sec. It is clear, therefore, that integrated rate constants should be used with care at low percentage conversions, or under strong vibration–dissociation coupling conditions. The results of reducing the integration step length do not otherwise affect the numerical data presented in this paper to any significant extent, nor do they affect any of the conclusions.

D. Conclusions

The use of the iterative matrix technique of Rush and Pritchard,[8] as developed in the preceding paper,[3] has led to about a 10^6-fold expansion of the accessible time scale for a reaction such as this one. For the most part, this is due to the fact that the first term in eq I(23) dominates the solution, and that the nonlinear terms are in effect a relatively small perturbation. It is our belief that Tables III and VI represent acceptable solutions for the hypothetical experiments described in this paper, not only because of the tests of accuracy imposed,[3] but also because of the internal consistency of the distribution functions and of the rate constant data, and the behavior of the entropy and its derivatives; there is not space to call attention to all these details, but a leisurely inspection of Tables III–VIII will reveal many of them.

A complete calculation of the rate of dissociation or recombination of a molecule under highly dilute conditions, and the temperature coefficients of those rates, requires a knowledge of a set of transition probabilities such as those in Table II, for each temperature under consideration. These probabilities are not known at this time, but, nevertheless we believe that on the basis of an intuitively reasonable set, we have come to a qualitative understanding of the dissociation process for a diatomic molecule, owing mainly to the fortunate circumstance that the qualitative behavior is relatively insensitive to these probabilities[35] and is in fact dominated by statistical-mechanical considerations.

In future work it should be possible to make a reasonable assessment of the various effects that have had to be neglected in this calculation, *e.g.*, those associated with the inclusion of *V–V* transitions, with the explicit inclusion of rotational states, with the inclusion of bound MX levels, with an increase in the nuclear masses, etc., although it will still need some considerable development of the techniques described here to achieve a complete description of the dissociation–recombination process.

Dedication. It is a pleasure for us to dedicate this account of our work to the memory of the late Winston Danae Walters.

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(34) G. H. Hardy, J. E. Littlewood, and G. Polya, "Inequalities," Cambridge University Press, London, 1934.

(35) T. Carrington, *J. Chem. Phys.*, **35**, 807 (1961).