Table III. Rate Constant and Cross-Section Values for Quenching of Hg 6($^3P_1$) Atoms by Rare Gas Atoms[a]

	k_2, l. mole^{-1} sec^{-1} × 10^{-9}	σ^2, Å^2 a	b	Rel emission intensities with filter 1	I(filter 1)/I(filter 2)
He	5.9	0.25	0.20	5.4	2.7
Ne	3.9	0.35	0.27	4.2	2.5
Ar	5.8	0.70	0.32	6.0	2.7
Kr	5.5	0.88	0.34	5.9	2.9
Xe	3.1	0.59	0.12	7.2	...

[a] The error and reproducibility of measurements are within a factor of 2.

+ Hg system which has been shown to follow third-order kinetics.[20]

Turning now to the potential energy calculations, neither our results on the Hg–Ar, Hg–Kr, and Hg–Xe molecules nor the results reported by various authors on the Hg–Ar and Hg–He molecules[21,23] do seem to corroborate the crossing mechanism. Also, if crossing of the ground state with either of the two excited states correlating with the Hg $^3P_1$–noble gas atom occurs, production of some Hg $^3P_0$ atoms would be expected because the state correlating with the Hg $^3P_0$–noble gas atom should always lie between the ground state and the states correlating with Hg $^3P_1$–noble gas atom. Thus the absence of metastable atoms may be taken as additional evidence against the crossing mechanism of quenching.

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(23) J. Szudy, *Acta Phys. Polon.*, **29**, 605 (1966); **30**, 721 (1966); **32**, 359 (1967).

The Master Equation for the Dissociation of a Dilute Diatomic Gas.[1] I. A Method of Solution

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Abstract: The master equation representing the dissociation–recombination kinetics of a dilute diatomic gas can be reduced to a system of inhomogeneous nonlinear Volterra integral equations of the second kind. Accurate solutions of these equations can be obtained using the self-consistent matrix iteration procedure proposed by Rush and Pritchard, under certain relatively unrestrictive conditions.

In setting up the "master equation" to represent the dissociation–recombination kinetics for a diatomic gas, three fundamental assumptions are implicit: (i) time must be considered as a continuous variable; (ii) the duration of the collisions which lead to transitions between states described in the equation must be infinitesimal compared with the time scale under consideration; (iii) the initial distribution of particle trajectories must be such that the distribution of first collision times is completely random. Thus, it is clear that the solutions of the master equation can only be valid at times which are long compared to the average time between collisions, and any attempt to deal with shorter times must appeal to more sophisticated treatments associated with the names of Bogoliubov and others.[2] We will assume in this work that the master equation gives a satisfactory representation of the dissociation–recombination kinetics of a diatomic gas.

We consider an idealized experiment in which a shock wave is passed through a mixture consisting of diatomic molecules X_2 and inert gas molecules M originally at a temperature of T_0. The heating process is assumed to be instantaneous, occurring at time $t = 0$, and after it has happened, the gas is considered to have an equilibrium distribution of translational energies corresponding to a temperature T_0', but to still have internal energies characteristic of T_0. Equilibration between the internal and the translational degrees of freedom then proceeds until a final equilibrium temperature T is reached. This takes place through a series of processes of the type

$$M + X_2(v,J) \rightleftharpoons M + X_2(v',J') \qquad (1)$$

and

$$X_2(\nu,\omega) + X_2(v,J) \rightleftharpoons X_2(\nu',\omega') + X_2(v',J') \qquad (2)$$

which represent all the transitions among the rotation–vibration levels of X_2. In describing the dissociation step itself, we assume that this occurs through latent pairs, the concentrations of which are always taken to be in equilibrium with the instantaneous atom concentrations, *i.e.*

$$X_2^* \rightleftharpoons X + X \text{ with } [X_2^*] = \lambda[X][X] \qquad (3)$$

$$MX^* \rightleftharpoons M + X \text{ with } [MX^*] = \delta[M][X] \qquad (4)$$

Reference should be made to our previous work[3] for the definition of X_2^*, etc., and for the methods by which the equilibrium constants λ and δ can be calculated; it should be borne in mind that if X is an atom like H and

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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) E. G. D. Cohen in "Fundamental Problems in Statistical Mechanics," North Holland Publishing Co., Amsterdam, 1962.

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

M is an atom like He, $\lambda >>> \delta$. The dissociation–recombination steps are then represented by

$$M + X_2(v,J) \rightleftarrows M + X_2^* \rightleftharpoons M + X + X \qquad (5)$$

$$M + X_2(v,J) \rightleftarrows MX^* + X \rightleftharpoons M + X + X \qquad (6)$$

$$X_2(\nu,\omega) + X_2(v,J) \rightleftarrows X_2(\nu',\omega') + X_2^* \rightleftharpoons X_2(\nu',\omega') + X + X \qquad (7)$$

In each case, the three-body recombination reaction is described by two successive two-body reactions, the first an association leading to a latent pair, followed by a reaction leading to the bound state. Since the master equation approach assumes that all interesting collisions are of infinitesimal duration, no inconsistency is introduced by circumventing three-body collisions in this way.

There is now no difficulty in setting up the master equation for the series of reactions 1–7. However, since the computational methods do not yet exist for dealing with a general scheme involving reactions 2 and 7, we must for the time being omit them from the reaction scheme, and confine our attention to a highly dilute mixture of X_2 in M so that X_2–X_2 collisions can be ignored; at the same time the total pressure is considered to be sufficiently low that n body reactions [*i.e.*, $X_2 + (n - 1)M$] are entirely absent. Furthermore, we accept that M and X are sufficiently simple that the molecule MX has no bound vibrational states in order to avoid the complication of having a pair of coupled master equations; there is no real loss of generality in so doing, and such a situation probably exists in any case when X is an H atom and M is an He atom.[4] Finally, we ignore all possible radiative processes, *i.e.*, spontaneous emission and coupling of states *via* the radiation field, both of which could be quite important if we had chosen our diatomic to be a heteronuclear molecule XY instead of the homonuclear X_2. Denoting the populations of the n bound rotation–vibration states of X_2 by n_i [$i = 0, 1, \ldots, (n - 1)$], and the populations of X_2^*, X, and MX* by n_n, $n_{(n+1)}$, and $n_{(n+2)}$, respectively, the master equation becomes

$$\frac{\partial n_i}{\partial t} = [M]\Big\{\sum_j [W_{ij}n_j - W_{ji}n_i] + [\bar{W}_{in}n_n - \bar{W}_{ni}n_i] + \Big[\bar{W}_{i(n+2)}\frac{n^2{}_{(n+2)}}{\delta[M]^2} - \bar{W}_{(n+2)i}n_i\Big]\Big\} \qquad (8)$$

where W_{ij} is the probability per unit time per unit concentration of a transition from state j to state i and the $\bar{W}_{ni}$ and $\bar{W}_{(n+2)i}$ represent similar quantities for processes 5 and 6, respectively; all the W's are averaged over the Boltzmann distribution of energies for M at the temperature concerned, and the $\bar{W}$'s are also averaged over the Boltzmann distribution of energies for X atoms. The terms under the summation sign represent all the transitions described by eq 1 and the second and third sets of square brackets represent processes described by eq 5 and 6, respectively. Then we also have

$$\frac{\partial n_n}{\partial t} = [M]\sum_j [\bar{W}_{nj}n_j - \bar{W}_{jn}n_n] + [\bar{W}_{n(n+1)}n^2{}_{(n+1)} - \bar{W}_{(n+1)n}n_n] \qquad (9)$$

$$\frac{\partial n_{(n+1)}}{\partial t} = [\bar{W}_{(n+1)n}n_n - \bar{W}_{n(n+1)}n^2{}_{(n+1)}] + [\bar{W}_{(n+1)(n+2)}n_{(n+2)} - \bar{W}_{(n+2)(n+1)}[M]n_{(n+1)}] \qquad (10)$$

$$\frac{\partial n_{(n+2)}}{\partial t} = [\bar{W}_{(n+2)(n+1)}[M]n_{(n+1)} - \bar{W}_{(n+1)(n+2)}n_{(n+2)}] + [M]\sum_j\Big[\bar{W}_{(n+2)j}n_j - \bar{W}_{j(n+2)}\frac{n^2{}_{(n+2)}}{\delta[M]^2}\Big] \qquad (11)$$

It can readily be seen that the sum of eq 8–11 represents the conservation conditions

$$\sum_{j=0}^{n+2} n_j = N; \qquad \sum_{j=0}^{n+2}\frac{\partial n_j}{\partial t} = 0 \qquad (12)$$

(as before[3] these simple expressions arise only if $n_{(n+1)}$ and $n_{(n+2)}$ are taken to be $^1/_2$[X] and $^1/_2$[MX*], respectively). The importance of rigorously maintaining these conservation conditions is crucial to the numerical calculations described in this and the succeeding paper (part II); technically, we should also include an equation in $\partial[M]/\partial t$ to maintain strict conservation in M, but we will not be troubled by this omission if $[M] \gg [X_2]$.

We will denote the equilibrium population of any state j at the final temperature T by $\tilde{n}_j$ and introduce a new variable

$$\xi_j = n_j/\tilde{n}_j \qquad (13)$$

Assuming detailed balancing at equilibrium, we have the following relations among the probabilities.

$$W_{ij}\tilde{n}_j = W_{ji}\tilde{n}_i$$
$$\bar{W}_{in}\tilde{n}_n = \bar{W}_{ni}\tilde{n}_i$$
$$\bar{W}_{(n+1)n}\tilde{n}_n = \bar{W}_{n(n+1)}\tilde{n}^2{}_{(n+1)}$$
$$\bar{W}_{(n+1)(n+2)}\tilde{n}_{(n+2)} = \bar{W}_{(n+2)(n+1)}[M]\tilde{n}_{(n+1)}$$
$$\bar{W}_{i(n+2)}\frac{\tilde{n}^2{}_{(n+2)}}{[M]\delta} = \bar{W}_{(n+2)i}[M]\tilde{n}_i \qquad (14)$$

Equations 8–11 then become

$$\frac{\partial \xi_i}{\partial t} = [M]\Big\{\sum_j W_{ji}[\xi_j - \xi_i] + \bar{W}_{ni}[\xi_n - \xi_i] + \bar{W}_{(n+2)i}[\xi^2{}_{(n+2)} - \xi_i]\Big\} \qquad (8a)$$

etc. Finally, making use of the equilibrium relations 3 and 4, which can be rewritten as

$$\xi_n = \xi^2{}_{(n+1)}$$
$$\xi_{(n+2)} = \xi_{(n+1)} \qquad (15)$$

and eliminating $\bar{W}_{n(n+1)}$ and $\bar{W}_{(n+1)(n+2)}$, eq 8a–11a eventually reduce to

$$\frac{\partial \xi_i}{\partial t} = [M]\Big\{\sum_j W_{ji}[\xi_j - \xi_i] + [\bar{W}_{ni} + \bar{W}_{(n+2)i}][\xi_n - \xi_i]\Big\} \qquad (8b)$$

$$\frac{\partial \xi_n}{\partial t} = \alpha(t)[M]\sum_j[\bar{W}_{jn} + \tilde{n}_j\tilde{n}_n^{-1}\bar{W}_{(n+2)j}][\xi_j - \xi_n] \qquad (9b)$$

$$\frac{\partial \xi_{(n+1)}}{\partial t} = \beta(t)[M]\sum_j[\bar{W}_{jn} + \tilde{n}_j\tilde{n}_n^{-1}\bar{W}_{(n+2)j}][\xi_j - \xi_n] \qquad (10b)$$

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(4) D. L. Bunker and N. R. Davidson, *J. Am. Chem. Soc.*, **80**, 5090 (1958); J. K. Cashion, *J. Chem. Phys.*, **48**, 94 (1968).

$$\frac{\partial \xi_{(n+2)}}{\partial t} = \gamma(t)[\mathrm{M}]\sum[\bar{W}_{jn} + \tilde{n}_j\tilde{n}_n^{-1}\bar{W}_{(n+2)j}][\xi_j - \xi_n] \tag{11b}$$

where

$$\alpha(t) = 2\tilde{n}_n\xi_{(n+1)}[2\tilde{n}_n\xi_{(n+1)} + \tilde{n}_{(n+1)} + \tilde{n}_{(n+2)}]^{-1}$$
$$\beta(t) = \tilde{n}_n[2\tilde{n}_n\xi_{(n+1)} + \tilde{n}_{(n+1)} + \tilde{n}_{(n+2)}]^{-1} \tag{16}$$
$$\gamma(t) = \beta(t)$$

There are several points of interest in this presentation of the master equation: (i) the quantities $\alpha(t)$, $\beta(t)$, and $\gamma(t)$ are implicitly functions of time, since they are all functions of $\xi_{(n+1)}$; (ii) the sum $[\tilde{n}_n\alpha(t) + \tilde{n}_{(n+1)}\beta(t) + \tilde{n}_{(n+2)}\gamma(t)] = \text{constant} = \tilde{n}_n$ as required by conservation; (iii) the driving force for any individual microscopic process $i \leftrightarrow j$ is directly proportional to the difference $[\xi_j - \xi_i]$.

We may now rewrite eq 8b–11b in a more compact form using matrix notation

$$\frac{\partial}{\partial t}\begin{bmatrix} \vdots \\ \xi_i \\ \vdots \\ \xi_n \\ \xi_{(n+1)} \\ \xi_{(n+2)} \end{bmatrix} = \left[\begin{array}{c|c|c|c} \mathbf{A}_{00} & \mathbf{A}_{01} & \mathbf{0} & \mathbf{0} \\ \hline \alpha(t)\mathbf{A}_{10} & \alpha(t)\mathbf{A}_{11} & 0 & 0 \\ \hline \beta(t)\mathbf{A}_{20} & \beta(t)\mathbf{A}_{21} & 0 & 0 \\ \hline \gamma(t)\mathbf{A}_{30} & \gamma(t)\mathbf{A}_{31} & 0 & 0 \end{array}\right]\begin{bmatrix} \vdots \\ \xi_i \\ \vdots \\ \xi_n \\ \xi_{(n+1)} \\ \xi_{(n+2)} \end{bmatrix} \tag{17}$$

where

$$\mathbf{A}_{00} \equiv [\mathrm{M}]\{(1 - \delta_{ij})W_{ji} - \delta_{ij} \times [\bar{W}_{ni} + \bar{W}_{(n+2)i} + \sum_k(1 - \delta_{ki})W_{ki}]\}$$
$$\mathbf{A}_{10} = \mathbf{A}_{20} = \mathbf{A}_{30} \equiv [\mathrm{M}]\{\bar{W}_{jn} + \tilde{n}_j\tilde{n}_n^{-1}\bar{W}_{(n+2)j}\} \tag{18}$$
$$\mathbf{A}_{11} = \mathbf{A}_{21} = \mathbf{A}_{31} \equiv -[\mathrm{M}]\sum_j[\bar{W}_{jn} + \tilde{n}_j\tilde{n}_n^{-1}\bar{W}_{(n+2)j}]$$
$$\mathbf{A}_{01} \equiv [\mathrm{M}]\{\bar{W}_{ni} + \bar{W}_{(n+2)i}\}$$

Note that $\mathbf{A}_{00}$, etc., is the transpose of the matrix which normally arises[3,5] when the equations are cast in terms of n_i or x_i instead of ξ_i. Thus at equilibrium, when all $\xi_i = 1$, and all $\partial\xi_i/\partial t = 0$, eq 17 and 18 reduce to the conservation conditions

$$\mathbf{A}_{00} \cdot \mathbf{1} + \mathbf{A}_{01} \cdot 1 = \mathbf{0}$$
$$\mathbf{A}_{10} \cdot \mathbf{1} + \mathbf{A}_{11} \cdot 1 = 0, \text{ etc.} \tag{19}$$

Having established the formal similarity of the master equation irrespective of whether process 5 or process 6 dominates the recombination (provided that MX has no bound levels), we can simplify the problem by dropping one of them, *viz.*, process 6 in the limit $[\mathrm{X_2}]/[\mathrm{M}] \rightarrow 0$; actually, at the level of approximation embodied in eq 23a below, we cannot distinguish kinetically between omitting (6) and scaling the $\bar{W}_{in}$. Deleting all terms with the subscript $(n + 2)$ from eq 16–18 leads to eq 20, where the A's are as defined in (18)

$$\frac{\partial}{\partial t}\begin{bmatrix} \vdots \\ \xi_i \\ \vdots \\ \xi_n \\ \xi_{(n+1)} \end{bmatrix} = \left[\begin{array}{c|c|c} \mathbf{A}_{00} & \mathbf{A}_{01} & \mathbf{0} \\ \hline \zeta(t)\mathbf{A}_{10} & \zeta(t)\mathbf{A}_{11} & 0 \\ \hline \Omega(t)\mathbf{A}_{20} & \Omega(t)\mathbf{A}_{21} & 0 \end{array}\right]\begin{bmatrix} \vdots \\ \xi_i \\ \vdots \\ \xi_n \\ \xi_{(n+1)} \end{bmatrix} \tag{20}$$

but with all the $(n + 2)$ terms omitted, and, with some rearrangement of (16)

$$\alpha(t) \rightarrow \zeta(t) = [1 + {}^1\!/\!_4(\lambda\tilde{n}_n\xi_n)^{-1/2}]^{-1}$$
$$\beta(t) \rightarrow \Omega(t) = [{}^1\!/\!_2(\lambda\tilde{n}_n)^{-1/2} + (4\xi_n)^{1/2}]^{-1} \tag{21}$$

again, $[\tilde{n}_n\zeta(t) + \tilde{n}_{(n+1)}\Omega(t)] = \text{constant} = \tilde{n}_n$, consistent with the conservation condition (12).

We can rewrite eq 20 in the symbolic form

$$\frac{\partial\xi(t)}{\partial t} = \mathbf{A}(t)\xi(t) \tag{22}$$

where there are two kinds of time dependence in $\mathbf{A}(t)$: one arises directly from the nonlinearity through eq 21, and the other is implicit since, as the relaxation proceeds, the temperature of the gas changes, thereby altering all the W_{ij}'s, etc., which contribute to $\mathbf{A}(t)$. For the purposes of this development, we will assume that this temperature change is small, so that the W_{ij}, etc., can be regarded as constant (this approximation is justified in paper II for the dissociation process, and we hope in later work to dispense with this limitation). Thus (22) becomes

$$\frac{\mathrm{d}\xi(t)}{\mathrm{d}t} = \mathbf{A}(t)\xi(t) = \mathbf{A}_{00}\xi(t) + \mathbf{\Gamma}[\xi_n(t)]\xi(t) \tag{22a}$$

where $\mathbf{\Gamma}[\xi_n(t)]$ is a time-dependent matrix consisting only of the last two rows and columns of $\mathbf{A}(t)$, and $\mathbf{A}_{00}$ is time independent. In integral form, this becomes

$$\xi(t) = e^{\mathbf{A}_{00}t}\xi(0) + \int_0^t e^{\mathbf{A}_{00}(t-t')}\mathbf{\Gamma}[\xi_n(t')]\xi(t')\,\mathrm{d}t' \tag{23}$$

which is a system of inhomogeneous nonlinear Volterra integral equations of the second kind.[6]

Following the normal procedure,[3,5] we symmetrize all but the last row and column of $\mathbf{A}(t)$ by a similarity transformation

$$\mathbf{B}(t) = \mathbf{E}\mathbf{A}(t)\mathbf{E}^{-1} \tag{24}$$

To be more specific, using the partitioned matrix notation, eq 25 is written: $\mathbf{E}_{00} \equiv \{\delta_{ij}\tilde{n}_j^{1/2}\}$, $\mathbf{E}_{11} = \delta_{in}\tilde{n}_n^{1/2}$,

$$\mathbf{B}(t) = \begin{bmatrix} \mathbf{E}_{00} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \zeta^{-1/2}(t)\mathbf{E}_{11} & 0 \\ \mathbf{0} & 0 & \mathbf{E}_{22} \end{bmatrix} \times \begin{bmatrix} \mathbf{A}_{00} & \mathbf{A}_{01} & \mathbf{0} \\ \zeta(t)\mathbf{A}_{10} & \zeta(t)\mathbf{A}_{11} & 0 \\ \Omega(t)\mathbf{A}_{20} & \Omega(t)\mathbf{A}_{21} & 0 \end{bmatrix}\begin{bmatrix} \mathbf{E}_{00}^{-1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \zeta^{1/2}(t)\mathbf{E}_{11}^{-1} & 0 \\ \mathbf{0} & 0 & \mathbf{E}_{22}^{-1} \end{bmatrix} =$$
$$\begin{bmatrix} \mathbf{E}_{00}\mathbf{A}_{00}\mathbf{E}_{00}^{-1} & \zeta^{1/2}(t)\mathbf{E}_{00}\mathbf{A}_{01}\mathbf{E}_{11}^{-1} & \mathbf{0} \\ \zeta^{1/2}(t)\mathbf{E}_{11}\mathbf{A}_{10}\mathbf{E}_{00}^{-1} & \zeta(t)\mathbf{A}_{11} & 0 \\ \Omega(t)\mathbf{E}_{22}\mathbf{A}_{20}\mathbf{E}_{00}^{-1} & \Omega(t)\zeta^{1/2}(t)\mathbf{E}_{22}\mathbf{A}_{21}\mathbf{E}_{11}^{-1} & 0 \end{bmatrix} \tag{25}$$

$\mathbf{E}_{22} = \delta_{i(n+1)}\tilde{n}^{1/2}{}_{(n+1)}$, and all the individual $\mathbf{A}$ and $\mathbf{E}$ matrices themselves are now time independent. Writing $\mathbf{B}_{ji} = \mathbf{B}_{ij} = \mathbf{E}_{ii}\mathbf{A}_{ij}\mathbf{E}_{jj}^{-1}$, etc., we perform an orthogonal transformation

$$\mathbf{H}'(t) = \tilde{\mathbf{S}}\mathbf{B}(t)\mathbf{S}$$

which diagonalizes the time-independent part of (25), *i.e.*, eq 26, where $\mathbf{H}_{00} = \tilde{\mathbf{S}}_{00}\mathbf{B}_{00}\mathbf{S}_{00}$ is now an nth order

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[5] E. W. Montroll and K. E. Shuler, *Advan. Chem. Phys.*, **1**, 361 (1958).

[6] F. G. Tricomi, "Integral Equations," Interscience Publishers, New York, N. Y., 1957.

$$\mathbf{H}'(t) = \begin{bmatrix} \mathbf{S}_{00} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & 1 & 0 \\ \mathbf{0} & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{B}_{00} & \zeta^{1/2}(t)\mathbf{B}_{01} & \mathbf{0} \\ \zeta^{1/2}(t)\mathbf{B}_{10} & \zeta(t)\mathbf{B}_{11} & 0 \\ \Omega(t)\mathbf{B}_{20} & \Omega(t)\zeta^{1/2}(t)\mathbf{B}_{12} & 0 \end{bmatrix} \times$$

$$\begin{bmatrix} \mathbf{S}_{00} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & 1 & 0 \\ \mathbf{0} & 0 & 1 \end{bmatrix} = \begin{bmatrix} \tilde{\mathbf{S}}_{00}\mathbf{B}_{00}\mathbf{S}_{00} & \zeta^{1/2}(t)\tilde{\mathbf{S}}_{00}\ \mathbf{B}_{01} & \mathbf{0} \\ \zeta^{1/2}(t)\mathbf{B}_{10}\mathbf{S}_{00} & \zeta(t)\mathbf{B}_{11} & 0 \\ \Omega(t)\mathbf{B}_{20}\ \mathbf{S}_{00} & \Omega(t)\zeta^{1/2}(t)\mathbf{B}_{21} & 0 \end{bmatrix} \quad (26)$$

diagonal matrix. Equation 26 is an exact representation of the master equation as it has been formulated here, in the sense that its substitution for $\mathbf{A}(t)$ in eq 22a and 23 will give an exact solution to the problem. One would then like to follow precedent[5] and define an evolution operator for the system, but this has the form of a rather intractable product of matrices whose elements are integral operators. It is at this stage that the approximation proposed by Rush and Pritchard[3] must be introduced.

The procedure adopted was as follows. For any time t under consideration, a guess was made at ξ_n, thereby defining $\zeta(t)$ and $\Omega(t)$ through eq 21. To define the evolution operator (see eq 29), it is necessary to generate the eigenvalues and eigenvectors of (26). The matrix 26 is very sparse, consisting of n diagonal elements H_{ii}, bordered to the right by one column and below by two rows, and the computational procedure took advantage of this fact by generating the eigenvalues and eigenvectors of $\mathbf{H}'(t)$ from $\mathbf{H}_{00}$ and $\mathbf{S}_{00}$ by iteration; this was a very considerable saving, since once the W_{ij} and $\bar{W}_{in}$ have been chosen, $\mathbf{H}_{00}$ and $\mathbf{S}_{00}$ become independent constants of the system. The evolution operator was consequently one appropriate to the specific time t, and it was allowed to operate on the initial distribution $\xi(0)$ to generate an approximation to $\xi(t)$. The newly calculated value of ξ_n was abstracted from this vector, and the process was repeated until two successive approximations to ξ_n were the same to 1 part in 10^6. This procedure is equivalent to assuming that $\mathbf{\Gamma}[\xi_n(t')]$ is a slowly varying function of time, and may be considered to have remained constant at its final value $\mathbf{\Gamma}[\xi_n(t)]$ throughout the trajectory. Thus eq 23 becomes

$$\xi(t) = e^{\mathbf{A}_{00}t}\xi(0) + \int_0^t e^{\mathbf{A}_{00}(t-t')}\mathbf{\Gamma}[\xi_n(t)]\xi(t')\,\mathrm{d}t' \quad (23a)$$

which has a unique solution for all $t > 0$ provided[7] that $\mathbf{A}(t)$ is continuous in the interval, and that $\mathbf{A}_{00}$ is negative definite; in fact, it can be shown not only that $\mathbf{A}_{00}$ is negative definite, but that $\mathbf{A}(t)$ is negative semidefinite *at all times* during the trajectory.[7,8] Writing

$$\mathbf{H}(t) = \begin{bmatrix} \mathbf{H}_{00} & \zeta^{1/2}(t)\mathbf{H}_{01} \\ \zeta^{1/2}\mathbf{H}_{10} & \zeta(t)\mathbf{H}_{11} \end{bmatrix} \quad (26a)$$

for the symmetric part (26), it can be seen by multiplying out that $\mathbf{H}'(t)$ can be diagonalized by the transformation[10]

$$\mathbf{D}' = \mathbf{X}\mathbf{H}'(t)\mathbf{Y}$$

i.e.

$$\mathbf{D}' = \begin{bmatrix} \tilde{\mathbf{Q}} & \mathbf{0} \\ -\mathbf{G}(t)\mathbf{Q}\mathbf{D}^{-1}\tilde{\mathbf{Q}} & 1 \end{bmatrix} \begin{bmatrix} \mathbf{H}(t) & \mathbf{0} \\ \mathbf{G}(t) & 0 \end{bmatrix} \begin{bmatrix} \mathbf{Q} & \mathbf{0} \\ \mathbf{G}(t)\mathbf{Q}\mathbf{D}^{-1} & 1 \end{bmatrix} = \begin{bmatrix} \mathbf{D} & \mathbf{0} \\ \mathbf{0} & 0 \end{bmatrix} \quad (27)$$

where $\tilde{\mathbf{Q}}\mathbf{H}(t)\mathbf{Q} = \mathbf{D}$.

Summarizing the transformations, we have

(i) $\dot{\xi}(t) = \mathbf{A}(t)\xi(t) = \mathbf{A}[\xi_n(t)]\xi(t)$ from eq 22a
(ii) $\mathbf{BE} = \mathbf{EA}$ from eq 24
(iii) $\mathbf{H}'\tilde{\mathbf{S}} = \tilde{\mathbf{S}}\mathbf{B}$ from eq 26
(iv) $\mathbf{D}'\mathbf{X} = \mathbf{X}\mathbf{H}'$ from eq 27
(v) $\mathbf{XY} = \mathbf{1}$ from eq 27

Using the first four of these equations, one can write

$$\mathbf{X}\tilde{\mathbf{S}}\mathbf{E}\dot{\xi}(t) = \mathbf{D}'\mathbf{X}\tilde{\mathbf{S}}\mathbf{E}\xi(t) \quad (28)$$

which is of the form $\dot{y}(t) = \mathbf{D}'y(t)$, it now being implicit that $\mathbf{X} = \mathbf{X}(t)$ is constant during the trajectory; this assumption is equivalent to the approximation of (23) by (23a). The required solution, therefore, making use of (v), is[11]

$$\xi(t) = \mathbf{E}^{-1}\mathbf{S}\mathbf{Y}e^{\mathbf{D}'t}\mathbf{X}\tilde{\mathbf{S}}\mathbf{E}\xi(0) \quad (29)$$

where $e^{\mathbf{D}'t}$ is a diagonal matrix whose elements are $e^{D'_{ii}t}$. Unfortunately, as shown below, $\mathbf{D}$ is singular, and transformation 27 cannot be accomplished because $\mathbf{X}$ and $\mathbf{Y}$ contain $\mathbf{D}^{-1}$. However, as soon as it is realized that we have more information than we require, it can easily be shown[7] that the solution follows from

$$\frac{\partial}{\partial t}\begin{bmatrix} \vdots \\ \xi_i \\ \cdot \\ \xi_n \end{bmatrix} = \left[\begin{array}{c|c} \mathbf{A}_{00} & \mathbf{A}_{01} \\ \hline \zeta(t)\mathbf{A}_{10} & \zeta(t)\mathbf{A}_{11} \end{array}\right] \begin{bmatrix} \vdots \\ \xi_i \\ \cdot \\ \xi_n \end{bmatrix} \quad (20a)$$

and the normalizing condition

$$\sum_{i=0}^{1+n}\tilde{n}_i\xi_i(t) = N \quad (12a)$$

The last row and column are omitted from all matrices occurring in eq 21–29 inclusive and the solution becomes

$$\xi(t) = \mathbf{E}^{-1}\mathbf{S}\tilde{\mathbf{Q}}e^{\mathbf{D}t}\mathbf{Q}\tilde{\mathbf{S}}\mathbf{E}\xi(0) \quad (29a)$$

which is entirely analogous to that proposed by Rush and Pritchard. Equation 29a only yields the ratios of the terms in the $\xi(t)$ vector, and their absolute magnitudes have to be established using the conservation condition 12a. What has happened in going from (20) to (20a) is that an undetermined transformation has been applied which annihilates the last row (and column) of $\mathbf{A}(t)$ in (20) without altering the rest of it.[12] Thus, in going from (29) to (29a) we should allow for this in constructing the back-transformation formula for $\xi(t)$. But the missing transformation in (29a) is simply effected by using (12a), and it is not necessary to include it formally.[7,9]

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(7) V. A. LoDato, Ph.D. Thesis, York University, Toronto, Canada, 1968.

(8) A second trivial solution exists[9] if $\xi_n(t) = 0$.

(9) D. L. S. McElwain, Ph.D. Thesis, York University, Toronto, Canada, to be submitted.

(10) We thank Dr. A. Wallis for pointing this out to us.

(11) E. A. Coddington and N. Levinson, "Theory of Ordinary Differential Equations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 76.

(12) It is possible to write a formal transformation very like eq 27, but like (27) this contains the inverse of a singular matrix, $\mathbf{A}(t)$, and so cannot be used for computational purposes.

Rush and Pritchard were unable to solve an equation analogous to (29a) because the eigenvectors in **Q** corresponding to the eigenvalues D_n and $D_{(n-1)}$ (those which essentially control the chemical part of the relaxation process) were insufficiently orthogonal to the remaining vectors. The formulation presented here has two major advantages over theirs. (1) They tried to solve directly for the population vector $n_i(t)$ which is itself very ill-conditioned, having elements ranging from the order of unity down to 10^{-12} (say for H_2 at 2000°K) at equilibrium; in solving for $\xi_i(t)$, all but one of the elements are of the order of unity in the interesting time range, and the effect of this is to load most of the ill-conditioning of the problem on to the vectors **Q**. (ii) They also tried to diagonalize $\mathbf{B}(t)$ at each cycle in the iteration, thereby losing control over the remaining cancellation problem. In the present approach, we could afford to spend a lot of time diagonalizing $\mathbf{B}_{00}$, the time-independent part of $\mathbf{B}(t)$. It was first reduced to tridiagonal form by the Householder method,[13] and the eigenvalues were located by bisection, suitably scaled;[14] the vectors were then found using Wallis' one-sweep *QR* with Newton shift;[15] finally, Rayleigh quotient iteration (using quadruple-length arithmetic in the inner products) was needed to improve the eigenvalues $\mathbf{H}_{00}$ and the eigenvectors $\mathbf{S}_{00}$ to double-length accuracy. Then, using a trial value for $\zeta(t)$, the bordered-diagonal matrix $\mathbf{H}(t)$ was constructed according to (26a); symmetric bordered-diagonal matrices, like symmetric tridiagonal matrices, possess the Sturm sequence property,[15] and the eigenvalues can readily be obtained by bisection, again suitably scaled.[14] The eigenvectors then follow from

$$[Q(t)]_{ki} = \zeta^{1/2}(t)h_{kn}[Q(t)]_{ni} \tag{30}$$

$$[Q(t)]_{ni} = \left[1 + \zeta(t)\sum_{k=0}^{n-1}\left(\frac{h_{kn}}{h_{kk} - D_i(t)}\right)^2\right]^{-1/2} \tag{31}$$

Thus, almost all the ill-conditioning (which is inherent in the problem by virtue of the range of numbers involved in any Boltzmann distribution function) is concentrated into eq 30 and 31, which can in principle be worked out in any length arithmetic that is necessary to obtain a solution. We did not find that the calculation of the time-independent $\mathbf{H}_{00}$ and $\mathbf{S}_{00}$ was particularly ill-conditioned using double-length arithmetic on an IBM machine (*i.e.*, approximately 16 decimal digits). However, it was essential to use quadruple-length arithmetic in part of the Rayleigh quotient iteration (as we have already noted); otherwise the determination of the $D_i(t)$ was too imprecise to yield satisfactory vectors *via* (30) and (31); the bordered-diagonal matrix itself was too ill-conditioned to be solved successfully by Rayleigh quotient iteration. We would recommend that at least 24–30 decimal places (depending on the machine available) be used in future work of this kind.

In conclusion, we anticipate the results described in the following paper in so far as they bear on the question of the accuracy of the approximation (23a). With the probabilities W_{ij}, etc., chosen for that calculation, equilibrium is achieved, to all intents and purposes, in a period of 5–10 sec. Rush and Pritchard[3] had shown that using conventional Runge–Kutta integration, solutions extending out to about 10^{-6} sec were feasible on a microsecond machine (Manchester University Atlas) if realistic error criteria were imposed.[16] In their formulation, the population most sensitive to error in the Runge–Kutta process was the top-most bound vibrational level, whereas, in the present formulation, the sensitive population in this time range is the atom concentration. This reformulation results in a moderate improvement in speed, to the extent that it was possible to integrate out to 10^{-6} sec in about 0.6 hr on a somewhat slower machine (IBM 360/50).

On the other hand, it was found that the self-consistent matrix iteration described in this paper would not converge (with the same W_{ij}) for times below 5×10^{-8} sec. The reason seems to be that the shorter the time, the more eigenvalues contribute to the expansion (29a), and the iterative process executes oscillations similar to those found by Rush and Pritchard, probably for similar reasons. Nevertheless, there is an overlapping time range in which both methods work, and so it is a simple matter to test the accuracy of the iterative application of (29a) against the direct Runge–Kutta integration of (20). If $\xi(0)$ at $t = 0$ is chosen to have all the molecules in one vibrational level (*e.g.*, $T_0 \approx 0$°K) and one tries to derive $\xi(t)$ in this time range *via* (29a), one finds that *all* the $\xi_i(t)$ *except* $\xi_n(t)$ agree to at least six decimal places, but that $\xi_n(t)$ itself is in error by as much as a factor of 4 (*i.e.*, factor of 2 in $\xi_{(n+1)}$ the atom concentration). This can be traced directly to the assumption involved in reducing (23) to (23a), *i.e.*, that $\Gamma[\xi_n(t')]$ can be regarded as having remained constant at its final value $\Gamma[\xi_n(t)]$ throughout the trajectory. Since, except at very early times,[9] $\xi_n(t)$ is rising roughly exponentially to a limiting value, the error in making this assumption will be the most serious during the early stages of the relaxation. This is confirmed by the fact that with the correct population for 10^{-7} sec as the starting vector, one can integrate directly to 10^{-6} sec, obtaining $\xi_n(t)$ in agreement with the Runge–Kutta solution to about 1%. Furthermore, integrating from 10^{-7} to 10^{-6} sec in five "equal steps" of $\Delta \log t = 0.2$ gave a value of $\xi_n(t)$ which was indistinguishable from the Runge–Kutta solution within the error criterion imposed on the latter. Realizing that as time progresses, the approximation (23a) must improve, we chose this particular prescription for the work described in the succeeding paper, taking the Runge–Kutta solution for $t = 10^{-6}$ sec as the starting

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(13) J. H. Wilkinson, "The Algebraic Eigenvalue Problem," Clarendon Press, Oxford, England, 1965.

(14) G. Hunter and H. O. Pritchard, *J. Chem. Phys.*, **46**, 2146 (1967).

(15) A. Wallis, D. L. S. McElwain, and H. O. Pritchard, *Intern. J. Quantum Chem.*, **3**, 711 (1969).

(16) The reason for this (and therefore the necessity for our using such a sophisticated computational technique) needs to be clearly understood, since many partial solutions of the master equation for relaxation of sets of oscillators, harmonic or anharmonic, have been obtained by Runge–Kutta techniques, or suitable improvements thereon.[17] In this particular case, we are interested in the rate of dissociation, which is principally determined by the populations of a few of the topmost vibrational levels. For the case of H_2 at 2000°K which is described in the following paper, these constitute some 10^{-11} of the total molecules present, and their concentrations can only be obtained with meaningful precision by imposing an impracticably small step-length in the integration process; on the other hand, there is no difficulty in calculating the dominant elements of $\xi(t)$ by these methods. In using the Runge–Kutta technique, the step-length has to be small[18] compared with the characteristic relaxation times (the D_i^{-1}) whereas in our iterative scheme, it only has to be short compared to the characteristic relaxation time of the nonlinear terms.

(17) C. E. Treanor, *Math. Computation*, **20**, 39 (1966).

(18) H. A. Antosiewicz and W. Gautschi in "Survey of Numerical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 314–346.

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.