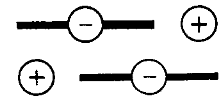
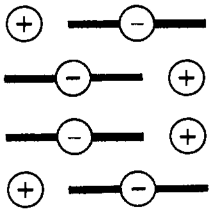
free quinoline·⁻ radical anion (in HMPA) has absorption maxima at 715 and 750 nm, whereas its dimer (formed in THF) absorbs at λ_{max} 360 nm. Therefore, the bathochromic shift observed in the dimerization of $PQ\cdot^-,Na^+$ is incompatible with covalent bonding.

The dimerization of the dimers (tetramerization) is an interesting phenomenon. The available thermodynamic data obtained in the THF system show that the reaction $2(PQ\cdot^-,Na^+) \rightleftharpoons (D^{2-},2Na^+)$ is exothermic and decreases the entropy of the system. This decrease may be accounted for by the loss of translational freedom of one particle. Apparently the degree of solvation (physical and chemical) of the dimer is comparable to that of the two monomers, a reasonable conclusion if the dimer is represented schematically by



and its agglomerate by



This implies a substantial desolvation of the reagents when dimers are converted into tetramers. This indeed is shown by our data.

The magnesium salts cannot tetramerize if Mg^{2+} is deeply squeezed into the sandwich of the dimer. This again seems to be the case.

Acknowledgment. The financial support of this study by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Vibration–Vibration Coupling in the Dissociation of a Diatomic Gas[1]

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Contribution from the Centre for Research in Experimental Space Science, York University, Downsview, Ontario, Canada. *Received December 31, 1969*

Abstract: Our previous formulation of the master equation for the dissociation of a dilute diatomic gas is extended to the nondilute case by the inclusion of V–V transitions. Using existing experimental and theoretical data for other molecules, estimates are made for the V–V transition probabilities in H_2. The master equation is solved for the dissociation of a series of M–H_2 mixtures at 2000°K, and the results are compared with those previously obtained for the same reaction at infinite dilution. The present solution is achieved by brute-force integration, continued through the transient period and out into the pseudosteady regime. Under weak V–V coupling conditions, the system is relatively well behaved, and it is possible to define (almost) unique values for the dissociation rate constants $k_{d.M}$ and k_{d,H_2}. However, when V–V transitions are very efficient, nonintegral rate laws of the form rate $= k_d{}^*[M]^x[H_2]^y$ with $x < 1 < y$ are obtained; the reaction orders x and y are constant only over limited concentration ranges, and the total order $m = (x + y)$ is always less than two.

We have shown recently, that it is possible, assuming a set of T–V transition probabilities, to solve the coupled vibration–dissociation relaxation problem for a gas resembling H_2 at infinite dilution[2,3] (equations and tables in these two papers will be designated hereinafter by prefixes I and II, respectively). This calculation neglected processes of the type

$$H_2(v_1J_1) + H_2(v_2J_2) \rightleftharpoons H_2(v_3J_3) + H_2(v_4J_4) \qquad (1)$$

$$H_2(v_1J_1) + H_2(v_2J_2) \rightleftharpoons H_2(v_3J_3) + H + H \qquad (2)$$

which are known to be important in any dissociation or recombination reaction, even at the highest experimentally feasible dilutions.[4] We have already alluded to the mathematical difficulties introduced by considering such V–V processes,[2] but a recapitulation of our earlier results[3] shows that it is possible to deduce the effect of including (1) and (2) in the relaxation process without being able to solve the complete problem.

We found[3] that, if H_2 was heated instantaneously from 0 to 2000°K, there were very rapid changes in the vibrational populations for a period lasting a little over 10^{-8} sec. At the end of this transient period,[5] a pseudosteady state was achieved, and this was maintained throughout the remainder of the dissociation process

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

(2) V. A. LoDato, D. L. S. McElwain, and H. O. Pritchard, *J. Amer. Chem. Soc.*, **91**, 7688 (1969). (We reproduce here for the reader's convenience a brief outline of the notation used in our previous work. n_i represents the population of state i in molecules/cc, $n_{(n+1)}$ the number per cc of dissociated molecules and n_n the concentration of transient pairs through which all *chemical* events proceed. P_{ji} is the probability per collision of a transition from state i to state j, $\bar{P}_{in}$ is the mean probability per collision that a transient pair will be deactivated to state i, and $\bar{P}_{(n+1)n}$ is the mean probability per collision that it will be dissociated into two atoms; the assumption that pairs are always in equilibrium with atoms implies that $\bar{P}_{(n+1)n}$ and $\bar{P}_{n(n+1)} \rightarrow \infty$ while still maintaining a ratio required by detailed balancing. $\bar{n}_i$, etc., represent equilibrium populations at the temperature of the experiment.)

(3) D. L. S. McElwain and H. O. Pritchard, *ibid.*, **91**, 7693 (1969).

(4) H. O. Pritchard in "Transfer and Storage of Energy by Molecules," Vol. 2, Wiley, London, 1969, pp 368–389.

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

(~1 sec under the conditions chosen), giving rise to a virtually unique phenomenological rate constant for dissociation. These observations refer to infinite dilution of the H_2 in an inert gas bath, the only condition under which a valid numerical procedure[2] exists for the solution of the relaxation problem throughout its whole trajectory. However, it was found that standard (Runge–Kutta-type) numerical integration techniques were good enough to integrate the relaxation equations through the transient period and into the beginning of the pseudosteady period—such an integration could be performed in 0.5–1 hr of computing time—and such numerical techniques are equally valid whether processes like (1) and (2) are present or not. In this paper, therefore, we describe the results of a brute-force calculation, analogous to our previous one, but including some selected V–V interchanges; each calculation was continued until the pseudosteady state was reached and the results are compared with those found earlier for the infinite dilution experiment.

The Master Equation with V–V Interchanges

In our previous calculation, the sheer size of the problem forced us to restrict our attention to the vibrational relaxation mechanism only, and to assume that the rotational and translational degrees of freedom were always in equilibrium with each other. For the time being, we must continue to make this assumption, and therefore rewrite (1) and (2) as

$$H_2(v = i) + H_2(v = j) \rightleftarrows H_2(v = k) + H_2(v = l) \quad (1a)$$

$$H_2(v = i) + H_2(v = j) \rightleftarrows H_2(v = k) + H + H \quad (2a)$$

In order to delineate those effects arising directly from the inclusion of processes 1a and 2a, and to separate them from other secondary effects, we make the following simplifying restriction. The calculations are performed on four different H_2–He mixtures such that the *initial* total number of particles is always the same (*i.e.*, $[H_2]_0 + [He]_0 = 3.5035 \times 10^{19}$ molecules/cc). Furthermore, H_2 and He are assumed to have equal T–V energy-transfer efficiencies (*viz.* $W_{ij} = ZP_{ij}$); and further still, it is assumed that each H atom produced by the dissociation has just one-half of the T–V efficiency of H_2 or He. In explanation, the second part of the restriction enables us to distinguish clearly the V–V coupling effect, which might be partly obscured if we had two parallel sets of processes with different T–V efficiencies; in addition, it is not very far from the truth to assume equal T–V efficiencies for H_2 and He. The third part of the restriction is less valid in principle,[6,7] but (a) it avoids having to change the relaxation matrix as the reaction proceeds, and (b) since we can only just integrate through the transient period up to a time when about 5×10^{-3}% of the reaction has occurred, the error introduced through this assumption is minute.

The following equations use the notation already established in our previous paper,[2] except that, of course, $P_{kl,ij}$ was not defined before, and with this particular ordering of the subscripts represents the probability per collision of process 1a in the *forward* direction. Thus, excluding recombination processes involving HeH and H_3 as before, eq I(8)–I(10) become

$$\frac{\partial n_i}{\partial t} = Z\Bigg[\{[H_2]_0 + [M]_0\}\Bigg\{\sum_{j=0}^{n-1}(P_{ij}n_j - P_{ji}n_i) + (\bar{P}_{in}n_n - \bar{P}_{ni}n_i)\Bigg\} + \sum_{j,k,l=0}^{n-1}(P_{ij,kl}n_kn_l - P_{kl,ij}n_in_j) + \sum_{j,k=0}^{n-1}(\bar{P}_{ij,kn}n_kn_n - \bar{P}_{kn,ij}n_in_j)\Bigg] \quad (3)$$

$$\frac{\partial n_n}{\partial t} = Z\Bigg[\{[H_2]_0 + [M]_0\}\Bigg\{\sum_{j=0}^{n-1}(\bar{P}_{nj}n_j - \bar{P}_{jn}n_n) + (\bar{P}_{n(n+1)}n_{(n+1)}{}^2 - \bar{P}_{(n+1)n}n_n)\Bigg\} + \sum_{\substack{i,j,k=0\\ i\leq j}}^{n-1}(\bar{P}_{kn,ij}n_in_j - \bar{P}_{ij,kn}n_kn_n)\Bigg] \quad (4)$$

$$\frac{\partial n_{(n+1)}}{\partial t} = Z\{[H_2]_0 + [M]_0\} \times \{\bar{P}_{(n+1)n}n_n - \bar{P}_{n(n+1)}n_{(n+1)}{}^2\} \quad (5)$$

with the additional detailed balancing relations to I(14)

$$P_{ij,kl}\tilde{n}_k\tilde{n}_l = P_{kl,ij}\tilde{n}_i\tilde{n}_j \quad (6a)$$

$$\bar{P}_{nj,kl}\tilde{n}_k\tilde{n}_l = \bar{P}_{kl,nj}\tilde{n}_n\tilde{n}_j \quad (6b)$$

Two subtle points should be noted here concerning the V–V transitions: (i) that in considering the conservation condition

$$\sum_{i=0}^{n+1}\partial n_i/\partial t = 0$$

[eq I(12)], one has to restrict the subscripts *in the last summation* of (3) to be $j \geq i$ only in order to avoid counting transitions twice; (ii) that in transitions where the reactants have subscripts $i = j$, the collision number Z is incorrect because it refers to collisions between unlike particles, and a correction factor must be absorbed into the $P_{kl,ii}$, etc. In terms of the variable $\xi_i = n_i/\tilde{n}_i$, these equations become

$$\frac{\partial \xi_i}{\partial t} = Z\Bigg[\{[H_2]_0 + [M]_0\}\Bigg\{\sum_{j=0}^{n-1}P_{ij}(\xi_j - \xi_i) + \bar{P}_{ni}(\xi_n - \xi_i)\Bigg\} + \sum_{j,k,l=0}^{n-1}\tilde{n}_jP_{kl,ij}(\xi_k\xi_l - \xi_i\xi_j) + \sum_{j,k=0}^{n-1}\tilde{n}_j\bar{P}_{nk,ij}(\xi_n\xi_k - \xi_i\xi_j)\Bigg] \quad (3a)$$

$$\frac{\partial \xi_n}{\partial t} = \zeta(t)Z\Bigg[\{[H_2]_0 + [M]_0\}\sum_{j=0}^{n-1}\bar{P}_{jn}(\xi_j - \xi_n) + \sum_{\substack{i,j,k=0\\ i\leq j}}^{n-1}\tilde{n}_k\bar{P}_{ij,kn}(\xi_i\xi_j - \xi_k\xi_n)\Bigg] \quad (4a)$$

As we have already shown,[2] an equation (5a) in $\partial\xi_{(n+1)}/\partial t$ is redundant (since $\xi_{(n+1)} = \xi_n{}^{1/2}$), provided that the right-hand side of (4a) is multiplied by the factor $\zeta(t)$ as defined in eq I(21). Finally, assuming the temperature change to be sufficiently small that the transition probabilities do not change during the reaction, we replace the partial derivatives in (3a) and (4a) by ordinary derivatives.

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(6) I. R. Hurle, P. Mackey, and J. L. J. Rosenfeld, *Ber. Bunsenges. Phys. Chem.*, **72**, 991 (1968).

(7) J. E. Bennett and D. R. Blackmore, *Proc. Roy. Soc., Ser. A*, **305**, 553 (1968).

Enumeration of V–V Resonances

It is now well established[4] that a process such as (1a) has quite a high probability if the vibrational energy content of the reactants is the same as that of the products; also, as the process departs from exact resonance by an energy $\Delta\epsilon_v$, the probability falls off logarithmically with increasing $\Delta\epsilon_v$. As a rough guide, at a dilution of 1% H_2 in He, any process having $\Delta\epsilon_v \leq 100$ cm^{-1} would compete effectively with T–V processes among the lower vibrational levels, and if $\Delta\epsilon_v \leq 25$ cm^{-1} would probably compete effectively with almost any T–V process taking placed in the system.

In order to demonstrate the magnitude of this problem, we have taken the 301 bound rotation–vibration energy levels of H_2 calculated by Waech and Bernstein[8] and enumerated the processes of type (1) which are resonant to within any arbitrary amount $\Delta\epsilon_{v,J}$. The rather surprising result is that there are many thousands of such resonances—in fact there are over 2000 resonances within 1 cm^{-1}, about 350 with $\Delta\epsilon_{v,J} = 0.1$ cm^{-1}, and 27 exact resonances! The exact resonances are listed in Table I, not because they themselves have any special significance (the energy levels of Waech and Bernstein are only quoted to the nearest 0.1 cm^{-1}, so that small changes in the data will change the sets of quantum numbers for which exact resonance occurs), but because they illustrate very clearly, in our view, the kind of wholesale redistribution of rotational and vibrational energy that one has to consider. Many of these processes involve large changes in angular momentum, as shown in the last column of Table I; however, since, as far as we know, no satisfactory calculation has been done involving simultaneous changes of v and J, it would be premature at this stage to assume that the majority of these resonances can be neglected on the grounds of large angular momentum changes. In T–R processes, as in T–V processes, large changes in quantum number are unfavorable, but this could be simply a consequence of the large change in translational energy that has to occur; thus, while we are certain that VR–VR processes will be restricted by large values of $\Delta\epsilon_{v,J}$, it is not so clear that they will be restricted by large values of ΔJ.

Table I. Exact Resonances for Processes 1 and 2 Based on the Energy Levels of Waech and Bernstein[8]

v_1	J_1	v_2	J_2	v_3	J_3	v_4	J_4	$\|\Delta J\|$
11	3	14	3	12	3	12	4	1
5	23	12	1	9	16	10	10	2
1	30	12	1	8	17	8	17	3
5	22	13	0	11	7	11	11	5
5	20	11	12	6	18	7	20	6
1	29	12	3	3	25	13	0	7
2	28	12	10	7	20	11	11	7
9	11	14	3	11	0	13	7	7
11	9	13	3	12	1	14	3	8
11	11	13	1	13	0	13	4	8
9	16	11	9	11	12	12	4	9
3	27	13	0	12	7	12	10	10
7	16	13	4	11	2	12	7	11
4	23	13	6	7	17	14	0	12
11	10	12	9	12	6	14	1	12
3	25	12	8	11	7	11	10	16
8	18	11	6	12	1	13	0	23
6	19	9	16	11	3	13	7	25
4	25	7	19	11	10	12	8	26
0	30	11	10	10	8	14	1	31
1	30	14	3	14	0	14	2	31
2	27	7	18	11	1	12	8	36
0	30	8	17	11	3	13	5	39
2	27	4	24	11	1	13	6	44
5	22	12	6	6	19	Limit[a]		
11	1	13	3	8	13	Limit[a]		
12	1	12	4	11	1	Limit[a]		

[a] Limit = dissociation limit: many other exact resonances occur with continuum states having energy above the dissociation limit (see detailed discussion below).

We have already noted above that it is not feasible to solve the vibration–rotation–dissociation relaxation problem considering, in full, all 301 bound rotation–vibration levels. One could try to follow the previous calculations, but assign to each V–V transition a probability which is an average over all the rotational states involved, weighted according to their $(2J + 1)$ multiplicities. However, this approach fails because it is not possible to maintain the detailed balancing of the individual processes and the meticulous conservation of particles which we have previously found so necessary for an accurate solution of the problem. Hence, to make progress, we now perform a much more restricted calculation, ignoring the rotational relaxation problem altogether, and simply assigning to each *exothermic* V–V transition a probability which is a function of the energy surplus $\Delta\epsilon_v$, in the form[4, 9]

$$\log P = \log P_0 - 0.006\Delta\epsilon_v \tag{7}$$

Two cases are considered below, one called the weak coupling case where P_0 is taken to be 0.01; thus, at exact resonance the transition probability is 0.01 and falls to about 10^{-5} per collision as $\Delta\epsilon_v$ increases to 500 cm^{-1}. The other, which we call the strong coupling case, assumes $P_0 = 0.5$, so that P falls from 0.5 to 5×10^{-3} over the same range of $\Delta\epsilon_v$. In either case, the probabilities for the reverse (endothermic) processes follow from the detailed balance relations (6). To conserve computing time, only transitions having $\Delta\epsilon_v \leq 100$ cm^{-1} were included; these are listed in Table II, together with the assumed transition probabilities for the forward and reverse transitions. The calculations described in this paper, therefore, use the T–V transition probabilities listed[3] in Table II(II), augmented by either of these two representative sets of V–V probabilities.

The Relaxation

Calculations were performed for He/H_2 ratios of 100, 10, 1, and 0.5, and in this section we compare the distribution functions ξ with those obtained previously at a 1000:1 ratio (with V–V coupling excluded). The results which are tabulated all relate to a time $t = 10^{-7}$ sec, which is well into the pseudosteady regime. In all the dissociations discussed here, the time taken to achieve the pseudosteady state was between 2 and 3 $\times$ 10^{-8} sec, either in the absence of V–V transitions, or in their presence, weak or strong; clearly, under our conditions, the rate of vibrational equilibration is determined by T–V transition rates. Furthermore, if the dissociation steps themselves are omitted from the relaxation scheme, this is the same time that it takes the vibrational levels to reach equilibrium, and it is therefore correct to associate this time interval with the vibrational relaxation time; these observations are

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

(9) J. T. Yardley, *ibid.*, 50, 2464 (1969).

Table II. Assumed Sets of V–V Transition Probabilities for Processes 1a and 2a

$i + j$	$k + l$	$\Delta\epsilon_v$, cm^{-1} [a]	Weak coupling case		Strong coupling case	
			$P_{kl,ij}$	$P_{ij,kl}$	$P_{kl,ij}$	$P_{ij,kl}$
$v = 3 + v = 6$	$v = 1 + v = 9$	4	9.5×10^{-3}	9.5×10^{-3}	0.48	0.48
$v = 9 + v = 10$	$v = 7 + v = 14$	16	8.0×10^{-3}	8.0×10^{-3}	0.40	0.40
$v = 4 + v = 7$	$v = 1 + v = 13$	27	6.9×10^{-3}	6.7×10^{-3}	0.35	0.34
$v = 6 + v = 9$	$v = 4 + v = 13$	29	6.7×10^{-3}	6.5×10^{-3}	0.34	0.33
$v = 11 + v = 12$	$v = 10 + v = 14$	68	3.9×10^{-3}	3.7×10^{-3}	0.20	0.19
$v = 6 + v = 6$	$v = 3 + v = 10$	79	3.3×10^{-3}	3.1×10^{-3}	0.17	0.16
$v = 8 + v = 11$	$v = 7 + v = 13$	79	3.3×10^{-3}	3.1×10^{-3}	0.17	0.16
$v = 5 + v = 10$	$v = 4 + v = 12$	90	2.9×10^{-3}	2.7×10^{-3}	0.15	0.14
$v = 3 + v = 7$	$v = 0 + v = 14$	100	2.5×10^{-3}	2.3×10^{-3}	0.13	0.12
$v = 5 + v = 11$	$v = 4$ + atoms	19	7.7×10^{-3}	*b*	0.39	*b*

[a] The processes are all exothermic in the direction $i + j \rightarrow k + l$. [b] The appropriate value follows from the application of eq 6b.

Table III. The Population Distribution Function, $\xi_i = n_i/\tilde{n}_i$, for the Dissociation of H_2 at 2000°K[a]

	[He]/[H_2] ratio				
	∞	100	10	1	0.5
$v = 0$	1.008320	1.002635	1.000868	1.000370	1.000320
$v = 1$	1.008320	1.002635	1.000868	1.000370	1.000320
$v = 2$	1.008320	1.002635	1.000868	1.000370	1.000320
$v = 3$	1.008320	1.002635	1.000868	1.000370	1.000320
$v = 4$	1.008319	1.002634	1.000868	1.000369	1.000320
$v = 5$	1.008316	1.002631	1.000865	1.000366	1.000316
$v = 6$	1.008295	1.002610	1.000843	1.000345	1.000295
$v = 7$	1.008177	1.002493	1.000726	1.000227	1.000177
$v = 8$	1.007635	1.001954	1.000190	0.999693	0.999644
$v = 9$	1.005374	0.999706	0.997947	0.997465	0.997422
$v = 10$	0.997298	0.991677	0.989940	0.989496	0.989467
$v = 11$	0.973116	0.967633	0.965960	0.965634	0.965648
$v = 12$	0.880944	0.875991	0.874558	0.874672	0.874849
$v = 13$	0.641557	0.637993	0.637296	0.639103	0.639924
$v = 14$	0.289881	0.288458	0.289663	0.298036	0.301433
Pairs	2.722×10^{-14}	2.690×10^{-13}	2.474×10^{-12}	1.385×10^{-11}	1.860×10^{-11}
Atoms	1.650×10^{-7}	5.187×10^{-7}	1.573×10^{-6}	3.721×10^{-6}	4.312×10^{-6}

[a] Weak V–V coupling case, time = 10^{-7} sec.

therefore consistent with our earlier remark[3] that in this calculation the coupling between vibration and dissociaton is relatively weak. Finally, as a check on the existence of a pseudosteady state at 10^{-7} sec, several of the integrations were taken out to 10^{-6} sec. The ξ_i for the bound levels remained unchanged to eight decimal places, and only the atom population had changed; furthermore, the dissociation rate constants calculated from the data at 10^{-7} and 10^{-6} sec were the same, confirming that the results for 10^{-7} sec really do represent the pseudosteady state.

(a) Weak V–V Coupling. The population distributions ξ for the four mixtures are compared with the infinite dilution calculation in Table III. It appears that each mixture has settled down to its own pseudosteady state, but this is an illusion owing to the fact that at each H_2 concentration, the equilibrium populations of atoms, and therefore the $\tilde{n}_i$, are different. We are reluctant to introduce another dimensionless parameter, but the situation is clarified by considering a new measure of the population distribution

$$\theta_i = \frac{\xi_i}{\xi_0} = \left(\frac{n_i}{n_0}\right) \Big/ \left(\frac{\tilde{n}_i}{\tilde{n}_0}\right) \tag{8}$$

One may interpret θ as the "degree of thermalization" of the level; the closer to unity is θ_i, the more nearly is the level i in thermal equilibrium with the "source" which is driving the reaction.[10] Comparison of the θ_i's in Table IV corresponding to the ξ_i's in Table III reveals that the distributions are really very similar indeed, with the two exceptions that the greater the H_2 concentration, (i) the greater the degree of thermalization, θ, of the upper vibrational levels, and (ii) the further advanced is the reaction. Both of these observations are a consequence of the additional pathways, listed in Table II, which connect the lower to the upper levels.

The phenomenological rate equation is assumed to be

$$\begin{aligned} \frac{-\mathrm{d}[H_2]}{\mathrm{d}t} &= \sum_{M_i = \mathrm{He,H_2,etc.}} [M_i]\{k_{\mathrm{d},M_i}[H_2] - k_{\mathrm{r},M_i}[H]^2\} \\ &= \sum_{M_i = \mathrm{He,H_2,etc.}} k_{\mathrm{d},M_i}[M_i]\{[H_2] - K^{-1}[H]^2\} \end{aligned} \tag{9}$$

However, at the very early times which we are considering, [H] is so small that the terms M_i = H and $K^{-1}[H]^2$ can be completely ignored, giving

$$\frac{-\mathrm{d}[H_2]}{\mathrm{d}t} = \sum_{M_i = \mathrm{He,H_2}} k_{\mathrm{d},M_i}[M_i][H_2] \tag{9a}$$

As we have already shown,[3] the left-hand side of (9) or (9a) is readily expressed in terms of the ξ_i and the transition probabilities, and by taking any pair of concentration ratios, one can therefore evaluate $k_{\mathrm{d,H_2}}$ and $k_{\mathrm{d,He}}$. All pairs lead to essentially the same values, *viz.*

$$k_{\mathrm{d,H_2}} = 4.290 \times 10^{-22}\ \mathrm{cm^3\ molecule^{-1}\ sec^{-1}}$$

$$k_{\mathrm{d,He}} = 4.196 \times 10^{-22}\ \mathrm{cm^3\ molecule^{-1}\ sec^{-1}}$$

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[10] Thus in a recombination, ξ_i should be scaled to the latent pair population function ξ_n to give a true measure of θ_i.

Table IV. The Degree of Thermalization, $\theta_i = \xi_i/\xi_0$, for the Dissociation of H_2 at 2000°K[a]

	[He]/[H_2] ratio				
	∞	100	10	1	0.5
$v = 0$	1.000000	1.000000	1.000000	1.000000	1.000000
$v = 1$	0.999999	0.999999	0.999999	0.999999	0.999999
$v = 2$	0.999999	0.999999	0.999999	0.999999	0.999999
$v = 3$	0.999999	0.999999	0.999999	0.999999	0.999999
$v = 4$	0.999999	0.999999	0.999999	0.999999	0.999999
$v = 5$	0.999996	0.999996	0.999996	0.999996	0.999996
$v = 6$	0.999975	0.999975	0.999974	0.999974	0.999974
$v = 7$	0.999858	0.999858	0.999858	0.999856	0.999856
$v = 8$	0.999321	0.999321	0.999321	0.999323	0.999324
$v = 9$	0.997078	0.997078	0.997081	0.997096	0.997102
$v = 10$	0.989069	0.989070	0.989080	0.989130	0.989150
$v = 11$	0.965086	0.965090	0.965121	0.965276	0.965338
$v = 12$	0.873675	0.873689	0.873799	0.874348	0.874569
$v = 13$	0.636263	0.636316	0.636743	0.638867	0.639719
$v = 14$	0.287489	0.287700	0.289411	0.297926	0.301337
Pairs	2.700×10^{-14}	2.683×10^{-13}	2.472×10^{-12}	1.384×10^{-11}	1.859×10^{-11}
Atoms[b]	1.643×10^{-7}	5.180×10^{-7}	1.572×10^{-6}	3.721×10^{-6}	4.312×10^{-6}

[a] Weak V–V coupling case, time = 10^{-7} sec. [b] Since, from eq I(15) $\xi_n = \xi_{(n+1)}{}^2$; *i.e.*, $\theta_{(n+1)} = \xi_{(n+1)}/\xi_0{}^{1/2}$.

Table V. The Degree of Thermalization, $\theta_i = \xi_i/\xi_0$ for the Dissociation of H_2 at 2000°K[a]

	[He]/[H_2] ratio				
	∞	100	10	1	0.5
$v = 0$	1.000000	1.000000	1.000000	1.000000	1.000000
$v = 1$	0.999999	0.999999	0.999999	0.999999	0.999999
$v = 2$	0.999999	0.999999	0.999999	0.999999	0.999999
$v = 3$	0.999999	0.999999	0.999999	0.999999	0.999999
$v = 4$	0.999999	0.999999	0.999999	0.999999	0.999999
$v = 5$	0.999996	0.999996	0.999995	0.999994	0.999994
$v = 6$	0.999975	0.999974	0.999972	0.999966	0.999965
$v = 7$	0.999858	0.999856	0.999846	0.999818	0.999812
$v = 8$	0.999321	0.999323	0.999341	0.999407	0.999428
$v = 9$	0.997078	0.997096	0.997231	0.997692	0.997823
$v = 10$	0.989069	0.989129	0.989573	0.991010	0.991392
$v = 11$	0.965086	0.965274	0.966645	0.971011	0.972149
$v = 12$	0.873675	0.874340	0.879201	0.894584	0.898564
$v = 13$	0.636263	0.638836	0.657652	0.717305	0.732782
$v = 14$	0.287489	0.297818	0.372368	0.592516	0.643833
Pairs	2.700×10^{-14}	2.741×10^{-13}	2.928×10^{-12}	2.389×10^{-11}	3.464×10^{-11}
Atoms	1.643×10^{-7}	5.235×10^{-7}	1.711×10^{-6}	4.888×10^{-6}	5.885×10^{-6}
ξ_0	1.008320	1.002635	1.000868	1.000370	1.000320

[a] Strong V–V coupling case, time = 10^7 sec. (The values of ξ_0 are listed at the foot of each column, so that the ξ_i can be recovered simply from the product $\xi_i = \theta_i\xi_0$. *Cf.* also footnote *a* of Table IV.)

The latter is identical with the value of $k_{d,He}$ derived from the previous calculation in the absence of V–V transitions (second column of Tables III and IV). Thus, it is clear that under these conditions, it is possible to define uniquely all the rate constants occurring in the phenomenological equation. It is interesting to note, however, that because of the probabilities chosen, the direct V–V dissociation flux (*i.e.*, that due to the last process in Table II) is several orders of magnitude lower than the T–V dissociation fluxes for M_i = He and H_2. Thus, the flux coefficients r_{He} and r_{H_2} are equal, as they must be since we originally chose equal T–V probabilities for both types of collision, and for the four mixtures under consideration, they are 4.197, 4.205, 4.243, and 4.258 × 10^{-22} cm^3 molecule^{-1} sec^{-1}, respectively. This monotonic rise in r reflects the progressive change in the $\xi(t)$ or $\theta(t)$ vector with increasing H_2 concentration, an effect which becomes much more accentuated in the next calculation. The reason why k_{d,H_2} comes out to be greater than $k_{d,He}$ when we compare pairs of experiments is that the dissociation flux coefficients increase with [H_2] but not with [He], together with the fact that we constrain the total flux to obey the rate law (9a); thus, while at very early times in the infinite-dilution calculation, $k_d = r$, this is no longer the case as far as $k_{d,He}$ or k_{d,H_2} is concerned.

(b) Strong V–V Coupling. A much more severe perturbation of the dilute gas calculation is introduced by increasing all the V–V transition probabilities by a factor of 50 (*i.e.*, the second set in Table II). This corresponds to a situation where, at exact resonance, separation into products k and l, or reactants i and j, is equally likely. This is close to the upper limit of efficiency (not precisely the upper limit, because each vibrational state has been considered to have the same collision frequency Z, and on this basis, V–V probabilities slightly in excess of 0.5 are acceptable). The T–V probabilities were left unchanged, *i.e.*, Table II(II). The distributions ξ_i and θ_i are listed in Table V for the same four mixtures. In each case, the degree of thermalization of the uppermost levels is higher, and the reaction itself has advanced to an extent which reflects this additional population in the upper states. Also, the similarity between the pseudosteady distributions is less marked than it was in the weak V–V case. In consequence, it is now impossible to find a unique

Table VI. Kinetic Behavior of the Dissociation of H_2 at 2000°K under Strong V–V Coupling Conditions

$[He]/[H_2]$ ratio	R_d, molecule cm^3 sec^{-1}	x	y	$m = (x + y)$	r	k_d^*	$k_{d(m=2)}^*$
					cm^3 $molecule^{-1}$ sec^{-1} [b]		
100	5.156×10^{15}	0.976	1.020	1.996	4.24×10^{-22}	5.6×10^{-22}	4.7×10^{-22}
10	5.108×10^{16}	0.822	1.145	1.967	4.58×10^{-22}	3.1×10^{-21}	7.4×10^{-22}
1	1.333×10^{18}	0.41[a]	1.55[a]	1.96	5.58×10^{-22}	6.7×10^{-21}	1.1×10^{-21}
0.5	4.763×10^{18}	0.26[a]	1.68[a]	1.94	5.82×10^{-22}	1.4×10^{-20}	1.1×10^{-21}

[a] At high $[H_2]$, the values of x and y vary very markedly for quite small changes in [He] or $[H_2]$, and a more general form of the rate expression, *e.g.*, $R_d = k_d^*[He]^x[H_2]^y + k_d\dagger[H_2]^z$, is needed. [b] *N.b.*, when $(x + y) \neq 2$, these units need appropriate modification.

pair of rate constants which satisfy the phenomenological eq 9 or 9a; those values for $k_{d,He}$ and k_{d,H_2} obtained vary considerably depending on the pairs of experiments chosen for their determination.

In fact, it is not possible to fit the entire set of data to any simple rate law. However, in the neighborhood of each mixture, simulating the experimental technique of holding one component constant and varying the concentration of the other by a factor of two in each direction, and *vice versa*, good fits to a series of rate laws of the form

$$\frac{-d[H_2]}{dt} = k_d^*[He]^x[H_2]^y \qquad (10)$$

are obtained (*n.b.*, for the determination of x and y, the restriction of constant $[He]_0 + [H_2]_0$ was obviously not imposed). Such rate laws have been found by Bauer and coworkers for a number of reactions in recent years. The individual rate laws are shown in Table VI, and it is seen that x and y vary with gross changes in composition of the mixture, that $x < 1$ and $y > 1$, and that the total order $m = (x + y)$ deviates progressively from 2; these results are strikingly similar to the observations of Lewis and Bauer[11] for the rate of formation of $H_2 + D_2$ from HD. Again (see below for further discussion of this point) the M_i = He and H_2 dissociation fluxes are nearly equal, and the rate coefficients for these fluxes are shown in Table VI for comparison with k_d^*. It is clear that k_d^* is far from constant, but this is due in part to the progressive departure of the total order from $m = 2$; this is shown in the last column of the table as a less severe trend when m is forced to take the value of 2. Even so, while at high dilutions the bimolecular rate constant is close to r, there is a discrepancy of about a factor of two for the more concentrated mixtures. The significance of the quantities k_d^*, $k_{d(m=2)}^*$, and r is as follows. The dissociation flux R_d can be represented by a series of expressions like (10): k_d^* is the constant of proportionality if x and y are allowed, without constraint, to take their true phenomenological values; $k_{d(m=2)}^*$ is the constant if we arbitrarily scale x and y equally so that their sum shall be 2, and r is the constant if we make $x = y = 1$. In our view, the latter quantity, r, has the most "physical meaning", but (except in the special case discussed here where $r_M = r_{H_2}$) it is also the most awkward to extract from the experimental observations.

Other Possible Considerations

Examination of Table II shows that an exact resonance occurs between two bound states on the one hand, and one bound state and an energy near the continuum limit on the other. In fact, whenever two colliding hydrogen molecules have between them more than the dissociation energy within their internal degrees of freedom, such a resonance with some part of the continuum must always occur. If such resonant processes have very high probability, they therefore represent wide-open channels for dissociation (and conversely recombination) to occur. However, their importance is moderated by the fact that they are intrinsically high energy processes; *i.e.*, the chance of two such molecules colliding is less than the chance of a collision between two molecules having only just enough energy to dissociate, by a quantity of the order of the Boltzmann factor $e^{-(\epsilon_i+\epsilon_j-D_0)/kT}$. Thus, while such processes may play a part in the dissociation–recombination process, it is only necessary to consider at the moment what effects may arise from such resonances lying near the continuum limit. Another way of looking at it is that such a process will only contribute appreciably to the dissociation–recombination flux if one of the products is a pair of atoms close to the continuum limit and the other is a H_2 molecule *in its ground vibrational state.*

In order to test the effect of such a path, we have repeated both the above sets of calculations including another process, *viz.*

$$H_2(v = 5) + H_2(v = 5) \rightleftarrows H_2(v = 0) + H + H \qquad (11)$$

as an exact resonance; this was achieved by a slight adjustment of the $v = 5$ level to make it exactly $D_0/2$. In the weak V–V calculation, the effect on the flux was imperceptible. However, in the strong V–V case, the inclusion of (11) caused a slight reduction in the degree of thermalization, θ, around $v = 5$, and an increase of a factor of 4 in the rate of the reaction. Here, we appeal to experiment[12] and note that in the case of the dissociation of H_2, k_{d,H_2} is only, at most, a factor of 10 greater than $k_{d,M}$; one would expect it to be somewhat larger on the grounds that H_2 may be more efficient than an inert gas atom in T–V processes. Hence, we can say with a fair degree of confidence that processes such as (11), if they have high efficiency, are not a serious problem, since if there were n such efficient processes, k_{d,H_2} would be of the order of $4n$ times $k_{d,M}$; thus, while such processes undoubtedly do participate, we need not be unduly suspicious of them unless k_{d,H_2} is very much greater than $k_{d,M}$.

It would be interesting to observe the effect of V–V coupling upon the recombination process. However, although we have performed integrations out to 10^{-6} sec with both sets of probabilities, there are at this time so few molecules present that the population distributions are not significantly different from those already found for the infinite-dilution calculation.[3] The only

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(11) D. Lewis and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 5390 (1968).

(12) I. R. Hurle, 11th International Symposium on Cumbustion, Berkeley, Calif., 1967, p 827.

effect we could detect was with the inclusion of process 11 in the strong V–V coupling regime, when at 10^{-6} sec there was a slight enhancement (0.5%) of the $v = 0$ population at the expense of $v = 5$. Clearly, more work on the recombination problem is necessary.

Conclusions

In our work so far, we have paid no attention to the problem of obtaining agreement between our calculated rate constant and values which may be derived for the temperature of 2000°K from recent experimental determinations.[12,13] We proceeded in our previous paper[3] solely on the basis of theoretically (and occasionally intuitively) estimated T–V transition probabilities,[14] and in this paper, on the basis of V–V transition probabilities chosen in consideration of the known properties of such transitions.[4,9] Without performing these two "*ab initio*" calculations, one could not have known with certainty beforehand the kind of dependence on the transition probabilities that would emerge. It now appears that, except in the presence of processes such as (11), the whole relaxation is dominated by T–V transition probabilities.

We regard the exact solution of the infinitely dilute gas relaxation problem (which is now possible[2,3]) given a correct set of T–V transition probabilities, as being rather like the exact solution of the H_2 problem in quantum mechanics. Thus, in the weak V–V case, one can make a good "mental extrapolaton" from the dilute gas behavior to the real behavior, just as the early quantum chemist made a mental extrapolation from H_2 to say HF, or O_2 or CH_4; in the strong V–V case, one is on much more difficult ground, rather like trying to describe the bonding in NaCl or XeF_4 from what we know about H_2. Of course, we have not yet achieved an exact solution of the T–V problem, since the correct probabilities are not yet available—but to pursue the analogy, it is possible to make a good deal of progress in valence theory solely on the basis of good intuitive wave functions, like the LCAO wave function for H_2^+, or the Heitler–London wave function for H_2.

In this paper we have distinguished two extreme kinds of behavior, and it seems likely that the observed experimental behavior will lie within these limits. On the one hand, when V–V transitions are not very efficient, one has a relatively simple situation described, to all intents and purposes, by unique rate constants. However, we see the beginnings of a logical difficulty,[15] that the quantity k_{d,H_2} is largely determined by the T–V transition rate, but also contains a small acceleration component which is related to the change in pseudo-steady distribution caused by the V–V transitions. On the other hand, when V–V transitions are very efficient, these difficulties become accentuated, and eventually lead to marked deviations from the simple rate law, both as regards order in the individual reactants, and in the total order.

From an experimental point of view, it becomes clear that much more effort than hitherto has to be put into the determination of the order of the dissociation in each reactant. The occurrence of nonintegral rate laws may reasonably lead one to suspect that one is operating in the strong V–V (or more generally VR–VR) coupling regime; in consequence, the derived rate constants bear a very involved relationship to the rates of the elementary processes which one believes one is studying. One can forsee the situation that Arrhenius temperature coefficients are determined, in part at least, by a gradual change in reaction order with temperature, and that the observed "activation energy" is not related simply to the energy of any elementary process. The only hope of obtaining "meaningful rate constants" is to work at higher and higher dilutions, thereby eliminating the effect of V–V transitions.

Unfortunately, increasing dilution would suppress the key process proposed by Lewis and Bauer[11] for the reaction $2HD \rightarrow H_2 + D_2$, and the only convincing thread which can be used to sustain this mechanism is the fact that the total flux is *much higher* than can be accounted for by any other mechanism. A complete description of the latter process involves the solution of a set of three coupled master equations, but we hope that such a calculation may prove feasible in the not too distant future.

Acknowledgment. We wish to thank Mr. Leon Wagschal, who wrote the computer program for the enumeration of the V–V resonances.

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