

# THE THREE-BODY RECOMBINATION AND DISSOCIATION OF DIATOMIC MOLECULES: A COMPARISON BETWEEN THEORY AND EXPERIMENT\*

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The modified phase-space theory of reaction rates has been used to predict the three-body recombination and dissociation rate coefficients of the diatomic gas molecules:  $H_2$ ,  $N_2$ ,  $O_2$ ,  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ ,  $HF$ ,  $HCl$ ,  $CO$ , and  $NO$ , in the presence of argon as a collision partner. The ability of the theory to quantitatively predict and correlate both low-temperature recombination rate measurements and high-temperature dissociation rate measurements is substantial. The success of the theory clearly illustrates the importance of the weak attractive forces between the recombining atoms and argon atoms for recombination at low temperatures, the marked reduction in the rates at high temperatures due to nonequilibrium distributions in the vibrational state populations of the molecules, and the major contributions to reaction progress via electronically excited molecular states at all temperatures for such molecules as  $N_2$  and  $CO$ .

## 1. Introduction

In this paper we have used the modified phase-space theory of reaction rates, as developed by Keck and his co-workers<sup>1-4</sup> for three-body reactions, to predict the individual dissociation and recombination rate coefficients of a number of diatomic gases diluted in an argon heat bath.

We have adopted the phase-space theory approach because it represents the most general method of calculating the reaction rates of atomic and molecular systems whose interaction can be described by the motion of a representative point in the classical phase space of the reacting system. It can be shown that the more conventional classical reaction-rate theories, such as unimolecular decay theory,<sup>5</sup> absolute reaction rate theory,<sup>6</sup> and available energy theory,<sup>7</sup> are all special cases of the phase-space theory. For a general discussion of these points we refer to Keck.<sup>1</sup>

Provided that the interaction potential of the three-body system can be defined, the modified phase-space theory which we have used here enables calculations to be made of dissociation and recombination rate coefficients which do not contain arbitrary constants and undetermined

“steric factors.” Thus, when subsequent comparisons are made with reliable experimental measurements, it is usually possible to ascribe any significant disagreement between the theory and experiment to inadequacies in the assumed form of the basic three-body interaction potential. Such comparisons thus provide a method of making quantitative improvements to the interaction potentials.

As we shall demonstrate by our comparisons, we have been able to obtain substantial quantitative agreement between theory and experiment and have thus correlated low-temperature three-body recombination rate measurements (obtained, for example, using the “discharge-flow-tube” technique) and high-temperature “shock-tube” dissociation rate measurements for those cases where both types of data are available. The over-all success of the theory clearly illustrates the importance of: (1) the attractive Van der Waal’s forces between the recombining atoms and the argon atoms for recombination at low temperatures (such forces are, of course, invoked in the “relaxed complex” mechanism of recombination<sup>8-11</sup>); (2) the departure from an equilibrium distribution of the vibrational state populations<sup>3,12</sup> which, for either dissociation or recombination, occurs at an energy level on the order of  $kT$  below the dissociation limit; and (3) the possible major contributions to the overall reaction rate due to reaction progress via electronically excited molecular states.<sup>4</sup>

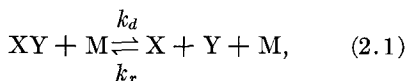
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The source experimental measurements we used in our comparisons were mainly suggested by recent review articles.<sup>13-16</sup> The particular cases we considered are the homonuclear diatomic gases  $H_2$ ,  $N_2$ ,  $O_2$ ,  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ , and the heteronuclear gases  $HF$ ,  $HCl$ ,  $CO$  and  $NO$ .

In this paper we shall not include the detailed development of the modified phase-space theory, since this can be found elsewhere.<sup>1-4</sup> A discussion of the theory and a complete summary of the working formulae has been given by Shui, Appleton, and Keck<sup>4</sup> for the particular case of the dissociation and recombination of nitrogen in an argon heat bath. We included in that paper a general account of the manner in which reaction progress via electronically excited states should be treated, together with a corrected version of the way in which departures from an equilibrium distribution in the vibrational state populations are allowed for. Thus, in Sec. 2 we shall give a brief summary of the working formulae and their physical interpretation, and devote the remainder of the paper to discussion of the comparisons between theory and experiment (Sec. 3), and our final conclusions (Sec. 4).

## 2. Theoretical Considerations

The type of reactions with which we are concerned are commonly written as



and are observed to proceed in accordance with the over-all rate equation

$$\begin{aligned} d[XY]/dt &= -k_d[XY][M] + k_r[X][Y][M] \\ &= -d[X]/dt = -d[Y]/dt, \end{aligned} \quad (2.2)$$

where  $k_d$  and  $k_r$  are, respectively, the over-all dissociation and recombination rate coefficients. For homonuclear diatomic molecules  $X_2$ , Eq. (2.2) becomes

$$\begin{aligned} d[X_2]/dt &= -k_d[X_2][M] + k_r[X]^2[M] \\ &= -d[X]/2dt. \end{aligned} \quad (2.3)$$

It is implied by the above rate equations that we restrict our attention to the calculation of reaction rates at times which are long by comparison with any "induction periods," i.e., the time intervals required to achieve close approximations to steady-state distributions in the internal energy

states of the molecules and atoms (see, for example, Ref. 17 for a discussion of the induction period due to vibrational relaxation). Therefore, both  $k_d$  and  $k_r$  are to be regarded as functions of temperature alone, and their ratio equal to an equilibrium constant. If, as we shall assume here,<sup>4</sup> each allowable electronic state of a particular species is present in the reacting system in its local equilibrium proportion relative to the total concentration of that species, then

$$\begin{aligned} k_d/k_r &= \sum_p Q(p) \sum_q Q(q) / \sum_m Q(m) \\ &= K_e(T) \end{aligned} \quad (2.4)$$

where  $Q(p)$  is the total particle partition function for atom  $X_p$  in electronic state  $p$ , and  $Q(q)$  and  $Q(m)$  are similarly defined for atom  $Y_q$  and molecule  $XY_m$ , respectively. The over-all rate coefficients are thus written in the forms

$$k_d = \sum_m k_d(m/p, q) Q(m) / \sum_m Q(m) \quad (2.5)$$

and

$$k_r = \sum_m k_r(m/p, q) Q(p) Q(q) / \sum_p Q(p) \sum_q Q(q), \quad (2.6)$$

where  $k_d(m/p, q)$  is the rate coefficient for dissociation of the molecule in electronic state  $m$ , to atoms in electronic states  $p$  and  $q$ , and  $k_r(m/p, q)$  is the corresponding recombination rate coefficient. We note that as a consequence of the Born-Oppenheimer separation, the specification of a particular molecular state automatically identifies the atomic states to which the molecule dissociates.

For most diatomic molecules and their atoms it is usually true that the ground-state partition functions, e.g.,  $Q(p=0)$ , are much greater than the partition functions of the first and higher excited states for temperature ranges of normal interest, and thus, the over-all rate coefficients may be approximately rewritten in the forms

$$k_d = \sum_m k_d(m | 0, 0) Q(m) / Q(m=0) \quad (2.7)$$

and

$$k_r = \sum_m k_r(m | 0, 0), \quad (2.8)$$

so that

$$k_d/k_r = Q(p=0) Q(q=0) / Q(m=0) \quad (2.9)$$

is the equilibrium constant based on ground-state concentrations only. One important exception for which the above approximate equations are not valid over the whole temperature range of our interest is the case of oxygen. The  $^3P$  "ground"-state oxygen atom actually consists of three states,  $^3P_2$ ,  $^3P_1$ , and  $^3P_0$  with slightly different energy levels: 0, 229°, and 326°K, and with corresponding degeneracies of 5, 3, and 1, respectively. Thus, at temperatures below about 1000°K, the exact equations (2.5) and (2.6) have been used here.

The modified phase-space theory enables us to calculate the individual recombination (or dissociation) rate coefficients,  $k_r(m|p, q)$ , in terms of what Keck<sup>1</sup> has called the "barrier rate" coefficient:  $k_r^B(m|p, q)$ . This latter quantity, which represents a rigorous upper bound to the actual rate coefficient, requires modification by a statistical correction factor ( $N/N_0$ ), and non-equilibrium correction factors ( $k/k_e$ ), to obtain  $k_r(m|p, q)$ .

The barrier rate is given in terms of the total one-way flow of points, representative of the three-body complex (X-Y-M), in the classical phase space across a suitably defined surface which separates the initial states of the system (the reactants) from their final states (the products). The phase-space surface which most logically separates molecules from atoms is the "barrier surface," which is defined by the constraints

$$E_{XY} - B_{XY} = 0: \quad E > 0, \quad (2.11)$$

where  $E$  is the total internal energy of the three-body system (X-Y-M),  $E_{XY}$  is the internal energy of the recombining atoms (X-Y), and  $B_{XY}$  is the height of the rotational energy barrier. For recombination, the product state is defined by  $(E_{XY} - B_{XY}) < 0$ , and the reactants by  $(E_{XY} - B_{XY}) > 0$ . By following this prescription, Keck<sup>1,2</sup> has derived the following expression for the barrier rate coefficient:

$$k_r^B(m|p, q) = 4\pi^2 f a^2 z_2^2 (z_2 - z_1) (8kT/\pi\mu_{XY})^{1/2} \times [1 - \exp(-B_m/kT)], \quad (2.12)$$

where  $f = g_{XYM}/g_{X_0}g_{Y_0}$  is the electronic degeneracy factor,  $\mu_{XY}$  the reduced mass of the molecule XY, and  $B_m$  the maximum height of the rotational barrier.

For the purpose of providing a simple physical explanation for the form of Eq. (2.12), we may point out that the factor  $4\pi z_2^2 (z_2 - z_1)$  is a molecular volume proportional to the number of atom

pairs (X-Y), close enough to recombine; whereas, the factor  $\pi a^2 (8kT/\pi\mu_{XY})^{1/2}$  is a rate constant proportional to the frequency at which the (X-Y) pairs are stabilized under the influence of the third-body M. The reason for the appearance of the reduced mass  $\mu_{XY}$  for the recombining atoms atoms in the velocity term rather than the reduced mass  $\mu_{XY,M}$  for collisions of (X-Y) with M, is that, in the "barrier rate," it is the rate of momentum transfer from M to (X-Y), rather than the collision rate of M with (X-Y), that controls the recombination. The additional factor  $[1 - \exp(-B_m/kT)]$  simply eliminates those atom pairs which cannot form bound molecules because of their excessive orbital angular momentum.

The characteristic lengths  $a$ ,  $z_1$ , and  $z_2$  are all temperature dependent and may be determined in terms of the characteristic potential parameters which are used to describe the interaction potential of the three-body system (X-Y-M). We have assumed that the interaction potential is given as the sum of two potentials

$$V_0 = V_{XY} + V_{iM}, \quad (2.13)$$

where  $V_{XY}$  is the potential of the recombining atoms (X-Y), and  $V_{iM}$  is the potential between one of the atoms and the third-body M;  $V_{iM} \equiv V_{XM}$  when the internuclear distance  $r_{XM}$  is smaller than  $r_{YM}$ , and  $V_{iM} \equiv V_{YM}$  when  $r_{XM} > r_{YM}$ . Keck has termed this the "dumb-bell" model of the interaction potential. In our calculations, we have used the Morse potential function

$$V(r) = U\{[1 - \exp[-\beta(r - r_e)]]^2 - 1\} \quad (2.14)$$

to represent both  $V_{XY}$  and  $V_{iM}$ , with appropriate suffices added to the potential parameters  $U$ ,  $\beta$ , and  $r_e$  to identify the particular two-body potential under consideration. Graphic solutions for  $a$ ,  $z_1$ , and  $z_2$  as functions of the appropriate potential parameters have been given elsewhere.<sup>4</sup> However, we should point out that the phase-space theory, in the form which we have used, tacitly assumes that all species, including the complexes X·M and Y·M, are present in their local equilibrium proportions, and, as a consequence, the major temperature dependence of the effective collision cross section ( $\pi a^2$ ), is determined by a factor  $\exp(U_{iM}/kT)$ .

Unfortunately, the barrier surface which is chosen to separate reactants from products in the phase space is not unique in the sense that representative point trajectories may cross and re-cross it several times. Since  $k_r^B$  is calculated

on the basis of the total one-way crossing rate, it does represent an upper bound to the actual rate.

Keck<sup>18</sup> has investigated this effect using Monte Carlo methods which sample phase-space trajectories that cross the "barrier" surface, and by integration of the classical equations of motion in both time-wise directions, has obtained a statistical determination of the fraction ( $N/N_0$ ), in which  $N$  is the number trajectories which result in a complete one-way reaction, and  $N_0$  the total number of trajectories sampled. Thus, we regard ( $N/N_0$ ) as a statistical correction factor which multiplies the value of  $k_r^B$  given by Eq. (2.12). Numerical values for ( $N/N_0$ ) can be found in Ref. 18, and semi-empirical formulae in Refs. 1 and 4.

The nonequilibrium correction factor which we have used here is based on the results of the investigation by Keck and Carrier<sup>3</sup> of the coupled vibration-dissociation-recombination process for a dilute mixture of diatomic molecules in a heat bath of inert collision partners. After the initial vibrational relaxation transient, it was found that for dissociation, the steady-state vibrational level population is very nearly Boltzmann except near the dissociation limit (within a few  $kT$  of the dissociation limit) where the levels are underpopulated; for recombination, the steady-state distribution is Boltzmann near the dissociation limit, but the lower levels are underpopulated. Because of this, the steady-state rate coefficients  $k_d$  and  $k_r$  are smaller than the equilibrium rate coefficients  $k_{de}$  and  $k_{re}$ , although their ratio is very nearly equal to the equilibrium constant; i.e.,

$$k_d/k_r = k_{de}/k_{re} = K_e(T). \quad (2.15)$$

By assuming a classical Morse oscillator to

represent the molecule, and an exponential form to represent the repulsive interaction between the collision partner and the molecule, Keck and Carrier solved the appropriate master equation to give a closed-form expression for the nonequilibrium correction factors ( $k/k_e$ ).

In Ref. 4 it was pointed out that when an attractive minimum exists in the two-body potentials  $V_{iM}$ , there are four contributions to the barrier rate coefficient, viz.,

$$k_r^B(m | p, q) = k_{rX+}^B + k_{rX-}^B + k_{rY+}^B + k_{rY-}^B \quad (2.16)$$

corresponding to four distinctly different configurations of the three-body complex for which the momentum transfer rate between (X-Y) and M are maximum. It is therefore necessary to evaluate a nonequilibrium correction factor, i.e., ( $k/k_e$ )<sub>i±</sub>, for each of these configurations, thereby obtaining an expression for the actual rate coefficient in the form

$$k_r(m | p, q) = [k_{rX+}^B (k/k_e)_{X+} + k_{rX-}^B (k/k_e)_{X-} + k_{rY+}^B (k/k_e)_{Y+} + k_{rY-}^B (k/k_e)_{Y-}] (N/N_0). \quad (2.17)$$

### 3. Comparisons Between Theory and Experiment

The potential parameters  $r_{eiM}$  for the Morse potential which describe the interactions between the separated atoms X and Y and the collision partner M, were first estimated from empirical rules, suggested by Bernstein and Muckerman,<sup>19</sup> which related  $r_e$  to the radii of the principal

TABLE I  
Interaction potential parameters  
(Morse potential:  $V_{iM}$ )

Species	From empirical rules			From curve-fitting	
	$r_e$ (Å)	$U$ (°K)	$\beta$ (Å <sup>-1</sup> )	$r_e$ (Å)	$U$ (°K)
H-Ar	2.91	130	1.44		
C-Ar	3.28	123	1.33		
N-Ar	3.18	200	1.49		380
O-Ar	3.10	220	1.44		
F-Ar	3.06	290	1.63		
Cl-Ar	3.39	384	1.41	2.4	900
Br-Ar	3.51	435	1.36	2.4	635
I-Ar	3.70	650	1.30	2.9	540

TABLE II  
Spectroscopic data for the molecules

Species	Molecular state	Dissociation products	Equilibrium separation $r_e$ (Å)	Dissociation energy $U$ (eV)	Electronic degeneracy factor $g_{xy}/g_x g_y$	Vibrational energy spacing $\omega$ (cm <sup>-1</sup> )
H <sub>2</sub>	$X\ ^1\Sigma_g^+$	$^2S + ^2S$	0.742	4.477	1/4	4161
N <sub>2</sub>	$X\ ^1\Sigma_g^+$	$^4S + ^4S$	1.10	9.76	1/16	2358
	$A\ ^3\Sigma_u^+$	$^4S + ^4S$	1.29	3.59	3/16	1461
O <sub>2</sub>	$X\ ^3\Sigma_g^-$	$^3P + ^3P$	1.21	5.12	1/27	1556
	$a\ ^1\Delta_g$	$^3P + ^3P$	1.22	4.14	2/81	1483
	$b\ ^1\Sigma_g^+$	$^3P + ^3P$	1.23	3.49	1/81	1405
	$C\ ^3\Delta_u^+$	$^3P + ^3P$	1.46	0.86	2/27	820
	$A\ ^3\Sigma_u^+$	$^3P + ^3P$	1.42	0.78	1/27	775
	$c\ ^1\Sigma_u^-$	$^3P + ^3P$	1.61	0.62	1/81	616
F <sub>2</sub>	$X\ ^1\Sigma_g^+$	$^2P + ^2P$	1.41	1.63	1/16	923
Cl <sub>2</sub>	$X\ ^1\Sigma_g^+$	$^2P_{3/2} + ^2P_{3/2}$	1.99	2.51	1/16	560
Br <sub>2</sub>	$X\ ^1\Sigma_g^+$	$^2P_{3/2} + ^2P_{3/2}$	2.28	1.97	1/16	323.2
	$A\ ^3\Pi_{1u}$	$^2P_{3/2} + ^2P_{3/2}$	(2.9)	0.22	1/8	170.7
I <sub>2</sub>	$X\ ^1\Sigma_g^+$	$^2P_{3/2} + ^2P_{3/2}$	2.67	1.542	1/16	215
	$A\ ^3\Pi_{1u}$	$^2P_{3/2} + ^2P_{3/2}$	(3.0)	0.07	1/8	44
HF	$X\ ^1\Sigma^+$	$^2S + ^2P$	0.917	5.91	1/8	4139
HCl	$X\ ^1\Sigma^+$	$^2S + ^2P$	1.275	4.43	1/8	2990
CO	$X\ ^1\Sigma^+$	$^3P + ^3P$	1.128	11.1	1/81	2170
	$a\ ^3\Pi$	$^3P + ^3P$	1.206	5.09	2/27	1744
	$a'\ ^3\Sigma^+$	$^3P + ^3P$	1.352	4.24	1/27	1231
	$d\ ^3\Delta$	$^3P + ^3P$	1.370	3.58	2/27	1153
	$e\ ^3\Sigma^-$	$^3P + ^3P$	1.383	3.33	1/27	1114
	$I\ ^1\Sigma^-$	$^3P + ^3P$	1.416	2.96	1/81	1064
	$A\ ^1\Pi$	$^3P + ^3P$	1.235	3.08	2/81	1516
NO	$X\ ^2\Pi$	$^4S + ^3P$	1.15	6.51	1/9	1876
	$a\ ^4\Pi$	$^4S + ^3P$	1.39	1.80	2/9	995

maxima in the radial distribution functions of the ground-state atoms.<sup>20</sup> The potential energy-well depths  $U_{iM}$  were first estimated by applying the Badger-Johnston relation<sup>19</sup> in the manner suggested by Bernstein and Muckerman. The remaining Morse potential parameters,  $\beta_{iM}$ , were obtained by setting  $2\beta_{iM} = 1/L_{iM}$ , where  $L_{iM}$  is the range of an effective exponential potential, given by the Mason-Vanderslice extrapolation

formula.<sup>21</sup> These estimates of  $r_{eIM}$ ,  $U_{iM}$ , and  $\beta_{iM}$  are summarized in Table I.

The spectroscopic data for the molecules which are required in the calculations are summarized in Table II. These data were mostly taken from Herzberg,<sup>22</sup> Gilmore,<sup>23</sup> Krupenie,<sup>24</sup> and the JANAF Tables.<sup>25</sup>

The source references for the experimental data have, to a large extent, been taken from the

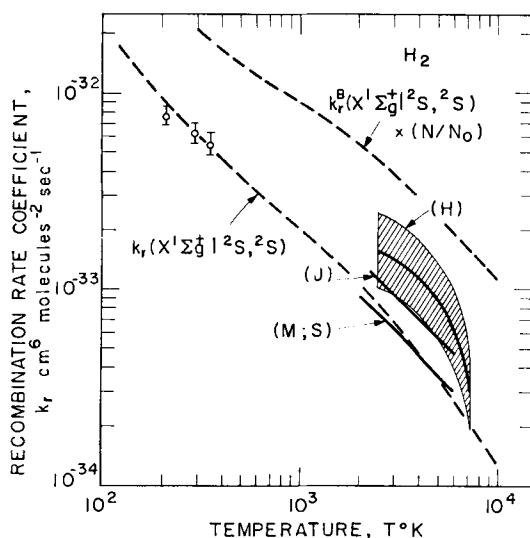


FIG. 1. Comparison between theoretical predictions of the recombination rate coefficient and experimental measurements for  $\text{H}_2$ , as a function of  $T$ ,  $\circ$ , Larkin and Thrush,<sup>26</sup> and Larkin<sup>27</sup>; (H), Hurle et al.<sup>28</sup>; (J), Jacobs et al.<sup>29</sup>; (M; S), Myerson and Watt,<sup>31</sup> and Sutton.<sup>30</sup> Dashed curves: see text, Sec. 3.1.

review articles cited previously, although we have attempted to include in our comparisons some more-recent investigations. Because of space limitations, we clearly cannot present a critical review of the many experimental investigations.

For those molecules where both low-temperature recombination rate data and high-temperature dissociation rate data are available, we have made the comparisons on the basis of the inferred recombination rate coefficients. For those molecules where only dissociation rate data are available, we have made the comparisons using the usual Arrhenius plots. Only for the case of oxygen have both methods of comparison been used. We again stress that the theoretical predictions were made on the assumption that argon was the collision partner which, in the majority of the experimental investigations chosen for comparison, was the case.

### 3.1 Hydrogen

Figure 1 shows our prediction of

$$k_r(X^1\Sigma_g^+ | ^2S, ^2S),$$

given by the lower dashed line, as compared with the direct recombination rate measurements<sup>26,27</sup> and the recombination rate coefficients inferred

from the high-temperature dissociation rate measurements for hydrogen.<sup>28-31</sup> The disagreement between our prediction and the highest high-temperature measurements by Hurle, Jones, and Rosenfeld<sup>28</sup> is about a factor of 2. However, our agreement with the experimental results of Sutton<sup>30</sup> and Myerson and Watt,<sup>31</sup> and the low-temperature recombination measurements of Larkin and Thrush<sup>26,27</sup> is excellent. Thus, in view of the possible experimental scatter, as indicated by the cross-hatched area which corresponds to the error estimate given in Ref. 28, we conclude that our prediction is good.

The upper dashed line in Fig. 1 shows our prediction of the equilibrium rate coefficient:  $k_r^B(X^1\Sigma_g^+ | ^2S, ^2S)(N/N_0)$ . By comparing this with the actual rate we see that the correction due to the nonequilibrium distribution in the vibrational state populations is significant over the entire temperature range of the experiments, but becomes most pronounced at high temperatures. The magnitude of the nonequilibrium correction was found to be similar for all of the

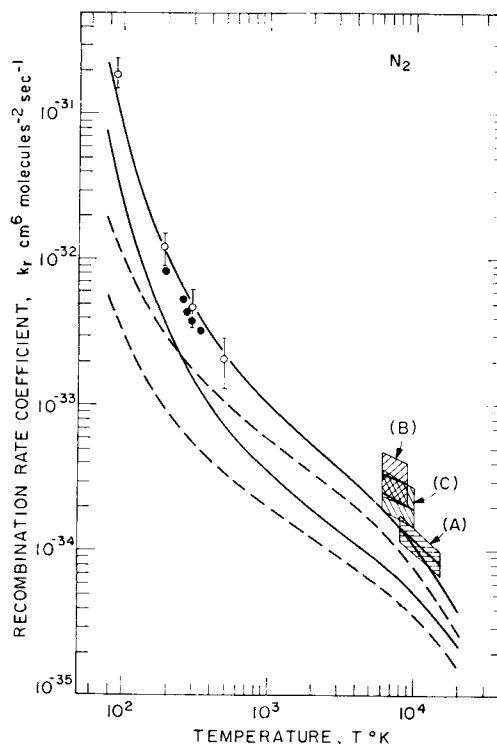


FIG. 2. Comparison between theoretical predictions of the recombination rate coefficient and experimental measurements for  $\text{N}_2$ , as a function of  $T$ .  $\circ$ , Clyne and Stedman<sup>33</sup>;  $\bullet$ , Campbell and Thrush<sup>32</sup>; (A) Appleton et al.<sup>36</sup>; (B) Byron<sup>34</sup>; (C), Cary.<sup>35</sup> Full and dashed curves: see text, Sec. 3.2.

homonuclear molecules considered, although we have not made the comparisons in the following figures in order to avoid confusion.

### 3.2 Nitrogen

We have treated the case of nitrogen in some considerable detail in a previous paper.<sup>4</sup> In that paper we discussed the experimental evidence<sup>32</sup> which indicated that direct recombination to the first excited state of the molecule exceeded that to the ground state by at least 50 per cent, and also included a discussion of the kinetic mechanism whereby the first excited state is populated and depopulated by collisions. Figure 2 is taken directly from Ref. 4. The upper dashed curve is our prediction of

$$[k_r(X^1\Sigma_g^+ | ^4S, ^4S) + k_r(A^3\Sigma_u^+ | ^4S, ^4S)],$$

and the lower dashed curve is the prediction of  $k_r(X^1\Sigma_g^+ | ^4S, ^4S)$ , alone. Both of these curves were calculated using the empirically derived potential parameters given in Table I. We have calculated the contributions to the over-all re-

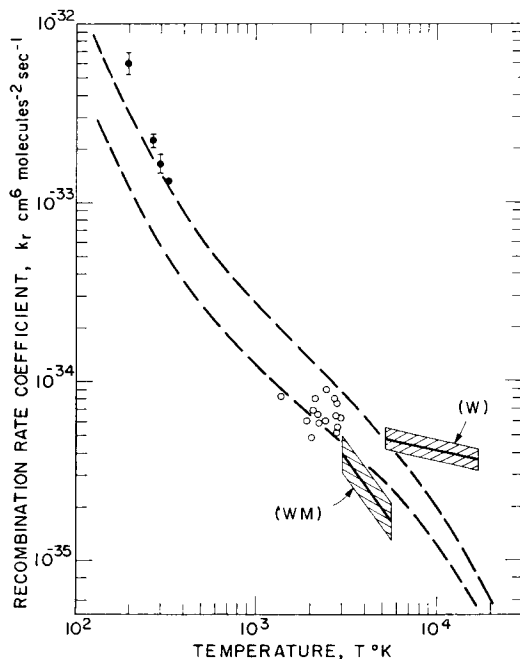


FIG. 3. Comparison between theoretical predictions of the recombination rate coefficient and experimental measurements for  $O_2$  as a function of  $T$ . ●, Campbell and Thrush<sup>37</sup>; ○, Wray<sup>39</sup>; (W), Wray<sup>41</sup>; (WM) Watt and Myerson.<sup>40</sup> Dashed curves: see text, Sec. 3.3.

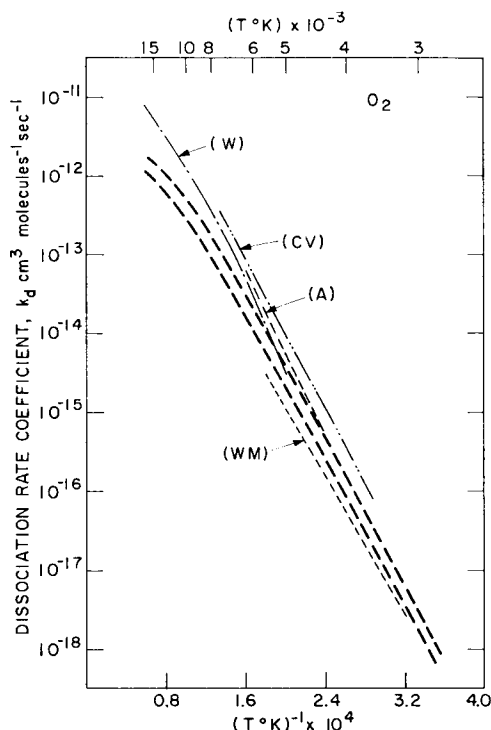


FIG. 4. Comparison between theoretical predictions of the dissociation rate coefficient and experimental measurements for  $O_2$ , as a function of  $T$ . (W), Wray<sup>41</sup>; (CV), Camac and Vaughan<sup>42</sup>; (A), Anderson<sup>43</sup>; (WM), Watt and Myerson.<sup>40</sup> Dashed curves: see text, Sec. 3.3.

combination rate coefficient due to recombination to other excited states, e.g.,  $^5\Sigma_g^+$ ,  $^3\Delta_u$ , etc., and have found them to be negligible over the entire temperature range considered, i.e., 90° to 20,000°K.

Since the temperature dependence of our prediction of  $k_r$  does not match that of the measurements due to Campbell and Thrush<sup>32</sup> and Clyne and Stedman<sup>33</sup> particularly well, and in view of our previous comment that the phase-space theory in the form used shows that the temperature dependence of  $k_r$  at low temperatures is primarily determined by the factor  $\exp(U_{NAT}/kT)$ , we increased the value of  $U_{NAT}$  (see Table I) and thereby obtained the predictions illustrated by the full curves in Fig. 2. By making changes in both of the other two parameters, i.e.,  $r_{eNAT}$  and  $\beta_{NAT}$ , theoretical values of  $k_r$  can be obtained which correlate any given set of low- and high-temperature data. Our preference for only changing  $U_{NAT}$ , resulted from our observation<sup>4</sup> that the high temperature prediction of  $k_d$  thus obtained agreed remarkably well with the measurements due to Appleton, Steinberg, and Liquornik,<sup>36</sup> and

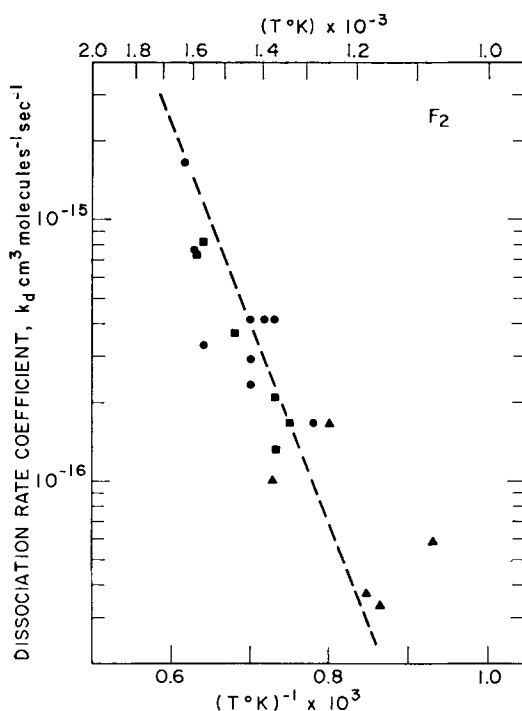


Fig. 5. Comparison between theoretical predictions of the dissociation rate coefficient for  $F_2$ , and the experimental measurements taken from Johnson and Britton.<sup>44</sup> Dashed curve: see text, Sec. 3.4.

because there is recent independent evidence from molecular beam scattering experiments due to Jordan, Colgate, Amdur, and Mason<sup>37</sup> which supports the value of  $\beta_{NAr}$  given by the Mason-Vanderslice extrapolation formula.<sup>21</sup>

### 3.3 Oxygen

Figure 3 shows our prediction of

$$k_r(X^3\Sigma_g^- | ^3P, ^3P),$$

lower dashed curve, and our prediction of the sum of the individual recombination rate coefficients corresponding to all the electronic states of oxygen listed in Table II, upper dashed curve.

Improved agreement with the temperature dependence of the low-temperature measurements due to Campbell and Thrush<sup>32</sup> could be obtained by increasing our estimate of  $U_{OAr}$ . However, this would also entail a reduction in our estimate of  $r_{eOAr}$  and a change in  $\beta_{OAr}$  for the theoretical value of  $k_r$  to still pass through the main body of the high-temperature data. We have not pursued this curve-fitting procedure in the case of oxygen, since we have rather arbi-

trarily assumed that each combination of the  $^3P_{2,1,0}$  states of the oxygen atoms interact without restriction along each of the potential energy curves of the molecule listed in Table II. We have thus violated the "noncrossing" rule of potential energy surfaces which may result in significant errors in our calculation of  $k_r$  at the low temperatures where the energy spacing between the  $^3P$  states are comparable with  $kT$ .

It is interesting to note that the recombination rates inferred from the dissociation rate measurements due to Watt and Myerson<sup>40</sup> agree quite well with the prediction of  $k_r(^3\Sigma_g^- | ^3P, ^3P)$ , lower dashed curve. This is indeed precisely what might be expected, since Watt and Myerson used the technique of atomic line-resonance absorption to monitor the production of oxygen atoms behind shock waves. Due to the high sensitivity of the technique, they were only able to measure the initial rate of dissociation over a period which, although encompassing the ground-state vibrational relaxation transient, quite possibly did not extend into the region where the higher electronic

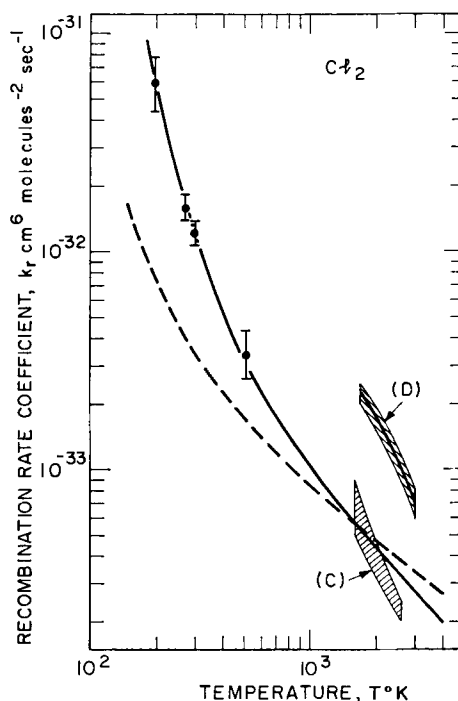


Fig. 6. Comparison between theoretical predictions of the recombination rate coefficient and experimental measurements for  $Cl_2$ , as a function of  $T$ . ●, Clyne and Stedman<sup>45</sup>; (D), Diesen and Felmlee<sup>46</sup>; (C), Van Thiel et al.,<sup>47</sup> Carabetta and Palmer,<sup>48</sup> and Jacobs and Giedt.<sup>49</sup> Full and dashed curves: see text, Sec. 3.4.

states assumed their local equilibrium concentrations.

Figure 4 shows an Arrhenius plot of the various dissociation rate measurements<sup>40-43</sup> together with our theoretical prediction of  $k_d$ . It is apparent that the theory underestimates some of Wray's<sup>41</sup> measurements and Camac and Vaughan's<sup>42</sup> measurements by about a factor of 2 to 3. However, it should be pointed out that, within the temperature range where the measurements overlap, there is disagreement between them of at least a factor of 2.

### 3.4 Fluorine, Chlorine, Bromine, and Iodine

An Arrhenius plot of the dissociation rate measurements for fluorine due to Johnson and Britton<sup>44</sup> is shown in Fig. 5, together with our prediction of  $k_d(X^1\Sigma_g^+ | ^2P, ^2P)$ . Although there is a relatively large scatter among the experimental data, the theoretical prediction does pass

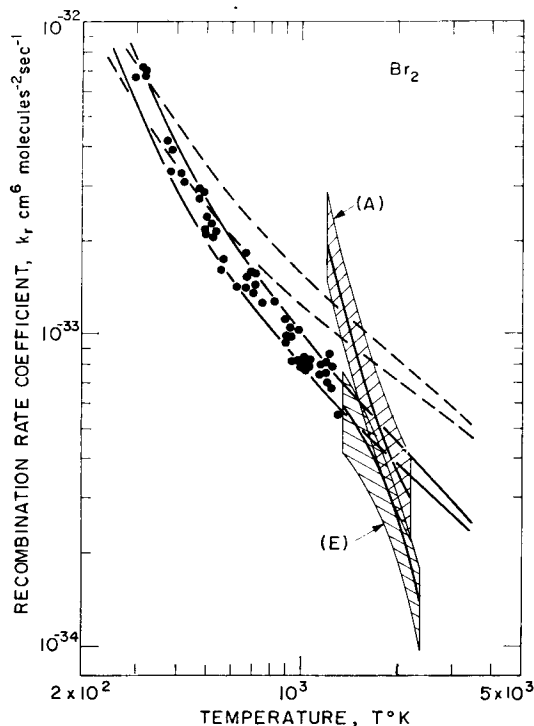


FIG. 7. Comparison between theoretical predictions of the recombination rate coefficient and experimental measurements for  $\text{Br}_2$ , as a function of  $T$ . ●, Ip and Burns<sup>11,50</sup>; (A), Johnson and Britton,<sup>53</sup> Warshay,<sup>54</sup> Britton,<sup>55</sup> and Palmer and Hornig,<sup>56</sup> as summarized by Ip and Burns<sup>51</sup>; (E), emission measurements of Boyd et al.<sup>52</sup> Full and dashed curves: see text, Sec. 3.4.

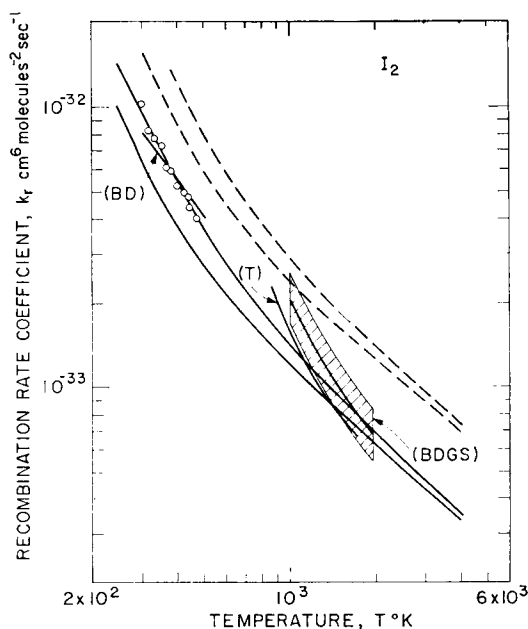


FIG. 8. Comparison between theoretical predictions of the recombination rate coefficient and experimental measurements for  $\text{I}_2$ , as a function of  $T$ . ○, Porter and Smith<sup>58</sup>; (BD), Bunker and Davidson<sup>57</sup>; (BDGS), Britton et al.<sup>59</sup>; (T), Troe and Wagner.<sup>60</sup> Full and dashed curves: see text, Sec. 3.4.

through the main body of the data and thus appears to be satisfactory.

The comparisons between the *a priori* theoretical predictions of the recombination rate coefficients (i.e., theoretical predictions obtained using potential parameters derived from empirical rules—dashed lines in Figs. 6–8) and the experimental measurements for  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  illustrate a definite trend. For the case of chlorine, Fig. 6, the theoretical prediction lies below the experimental data over the major portion of the temperature range and has a less-steep temperature dependence than that indicated by the combined measurements. On the other hand, Fig. 8, for iodine, shows that the *a priori* prediction of  $[k_r(X^1\Sigma_g^+ | ^2P_{3/2}, ^2P_{3/2}) + k_r(A^3\Pi_{1u} | ^2P_{3/2}, ^2P_{3/2})]$  is greater than the measurements by about a factor of 2, but exhibits a temperature dependence which is in reasonable agreement with the combined measurements. The comparison for the case of bromine, Fig. 7, appears to be an intermediate situation, i.e., the prediction of the recombination rate is greater than the bulk of the experimental data at temperatures above 300°K, but at lower temperatures it lies below an extrapolation of the experimental results.

Having recognized these trends and, again, in

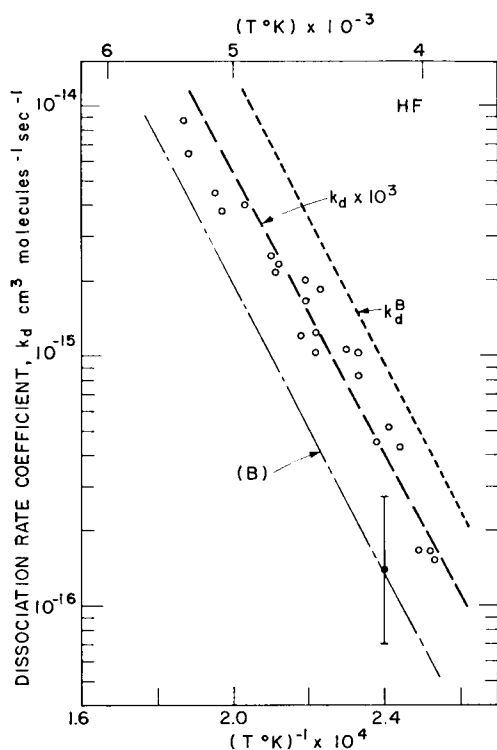


FIG. 9. Comparison between theoretical predictions of the dissociation rate coefficient and experimental measurements for HF, as a function of  $T$ .  $\circ$ , Jacobs et al.<sup>61</sup>; (B), Blauer.<sup>62</sup> Long dashed and short dashed curves: see text, Sec. 3.5.

view of our previous comment that the major temperature dependence of  $k_r$  is largely determined by the factor  $\exp(U_{iM}/kT)$ , at low temperatures, whereas, it is roughly proportional to  $r_{eiM}^2$ , independently of temperature, we adjusted the values of  $U_{iM}$  and  $r_{eiM}$  ( $i = \text{Cl, Br, I}$ ) as shown in Table I, to obtain the full theoretical curves illustrated in Figs. 6–8. It is apparent that this fitting procedure has enabled us to correlate a large fraction of the experimental data for dissociation and recombination of the halogens, and, as a consequence, we suggest that the derived potential parameters, particularly  $U_{\text{ClAr}}$  and  $U_{\text{BrAr}}$ , are more realistic than those given by the empirical rules.

The above curve-fitting procedure follows in much the same spirit as Porter<sup>10</sup> chose to view the binding energy of the relaxed complex  $\text{I}\cdot\text{M}$  as an adjustable parameter for correlating iodine recombination measurements, and more recently, as Ip and Burns<sup>11</sup> similarly chose to view the binding energy of the relaxed complex  $\text{Br}\cdot\text{M}$ , as an adjustable parameters for correlating their bromine recombination measurements. For the

$\text{I}\cdot\text{Ar}$  complex, Porter suggested  $U_{\text{I}\cdot\text{Ar}} \approx 500^\circ\text{K}$ , and for  $\text{Br}\cdot\text{Ar}$ , Ip and Burns suggested  $U_{\text{Br}\cdot\text{Ar}} \approx 450^\circ\text{K}$ , cr. Table I.

### 3.5 Hydrogen Fluoride and Hydrogen Chloride

The Arrhenius plots of the dissociation rates of hydrogen fluoride and hydrogen chloride, illustrated in Figs. 9 and 10, show that our predictions of the dissociation rate coefficients are much too low by comparison with the experimental measurements.<sup>61–65</sup> However, we have also plotted the barrier rate coefficients  $k_d^B(X^1\Sigma^+ | ^2S, ^2P)$ , which, although they are too large (as we should expect), nevertheless, have about the right temperature dependence. We believe that the reason our predictions of the rate coefficients underestimate the measured rates is that our estimate of the statistical correction factors  $(N/N_0) \lesssim 0.01$ , and the nonequilibrium correction factors  $(k/k_e) \approx 0.01$  are too small. The correlation formulae which we have used<sup>3,4,17</sup> to estimate the values of  $(N/N_0)$  and  $(k/k_e)$  were deduced using the

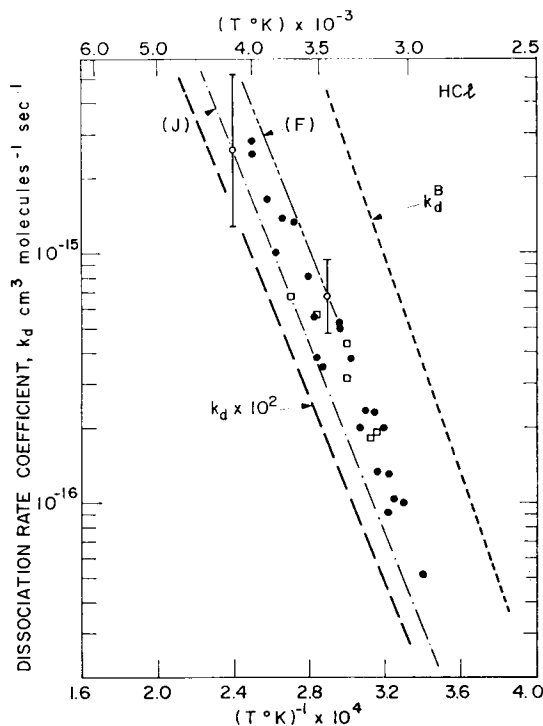


FIG. 10. Comparison between theoretical predictions of the dissociation rate coefficient and experimental measurements for HCl, as a function of  $T$ . Point measurements: Seery et al.<sup>65</sup>; (F), Fishburne<sup>63</sup>; (J), Jacobs et al.<sup>64</sup> Long dashed and short dashed curves: see text, Sec. 3.5.

results of Monte Carlo trajectory calculations and master equation solutions in which the recombining molecules and the collision partners had similar masses. We believe that the mechanics of reacting collision processes in which one of the recombining atoms has a very small mass is sufficiently different from those cases considered in Ref. 18, that the correlation formula is no longer valid. Further work on this problem is in progress.

### 3.6 Carbon Monoxide and Nitric Oxide

Figure 11 shows an Arrhenius plot of the measured dissociation rate coefficients<sup>66-69</sup> of carbon monoxide together with our predictions of  $k_d(X^1\Sigma_g^+ | ^3P, ^3P)$ , lower dashed curve, and  $\sum_m k(m | ^3P, ^3P)$ , upper dashed curve (see Table II for identification of the electronic states included). The prediction which includes all of the excited state contributions is nearly an order of magnitude greater than  $k_d(X^1\Sigma_g^+ | ^3P, ^3P)$  and, consequently, is in better agreement with

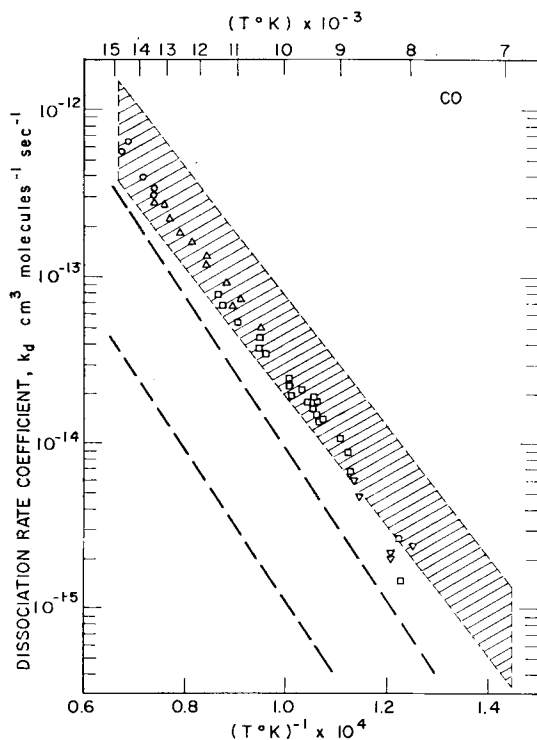


FIG. 11. Comparison between theoretical predictions of the dissociation rate coefficient and experimental measurements for CO, as a function of  $T$ . Point measurements: Appleton et al.<sup>69</sup>; Shaded area: Davies,<sup>66</sup> and Presley.<sup>67</sup> Dashed curves: see text, Sec. 3.6.

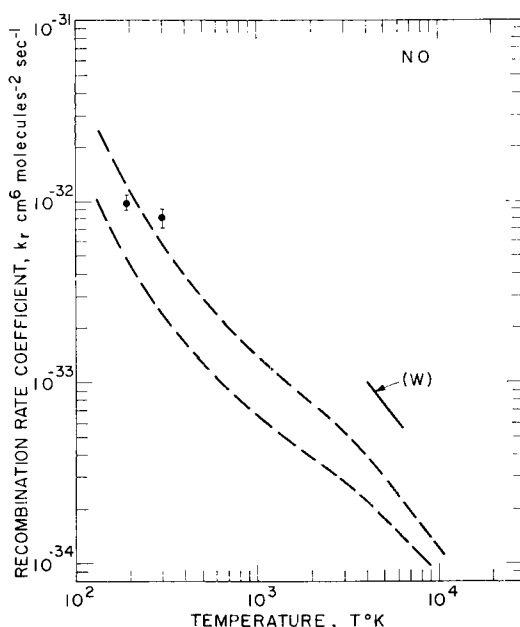


FIG. 12. Comparison between theoretical predictions of the recombination rate coefficient and experimental measurements for NO, as a function of  $T$ . ●, Campbell and Thrush<sup>38</sup>; (W), Wray and Teare.<sup>70</sup> Dashed curves: see text, Sec. 3.6.

the measurements. Small increases in either  $r_{eIM}$  or  $\beta_{iM}$  could be made which would allow the theoretical value of  $\sum_m k_d(m | ^3P, ^3P)$  to correlate quite well with the bulk of the experimental data. The fact that it does agree so well with the experimental measurements is quite gratifying, since Fairbairn<sup>68</sup> and Appleton, Steinberg, and Liquornik<sup>69</sup> (point values in Fig. 11) did observe an induction time immediately following the shock wave, prior to the onset of a steady-state dissociation, which they attributed to the time required to populate excited molecular states.

Figure 12 shows our predictions of

$$k_r(X^2\Pi | ^4S, ^3P),$$

lower dashed curve, and

$$[k_r(X^2\Pi | ^4S, ^3P) + k_r(a^4\Pi | ^4S, ^3P)],$$

upper dashed curve, together with the few experimental rate measurements for nitric oxide which are available.<sup>38,70</sup> The agreement is fairly good, although it would certainly be desirable to have more extensive measurements of the rates of this important molecule. Again, as in the case of CO, a slight increase in the value of  $\beta_{iAr}$  would

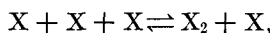
raise the high-temperature rate coefficients and place the theoretical predictions in closer agreement with Wray's dissociation rate measurements.<sup>70</sup>

#### 4. Conclusions

In the foregoing, we have demonstrated that modified phase-space trajectory calculations of the reaction rate coefficients of diatomic molecules in an argon heat bath are able to correlate both the very high- and low-temperature rate measurements. The exceptions to this conclusion appear to be those diatomic molecules which have disparate atomic masses, such as HF and HCl.

Apart from the recognition that reaction progress via excited molecular states is likely to be important in certain cases, e.g., N<sub>2</sub> and CO, the quantitative success of the theory is clearly dependent on prior knowledge of the interaction potential between the recombining atom pairs and the collision partner. However, on the basis of the comparisons presented here, we suggest that valid quantitative information on the interatomic potentials can be obtained from a proper synthesis of the phase-space theory and reliable experimental data obtained over a wide temperature range. Such a view is, of course, entirely in keeping with existing methods which have been widely used for deducing intermolecular potential information at thermal energies from measurements of transport properties.

Finally, we should point out that, for those cases where the collision partners are highly reactive, e.g.,



the "dumb-bell" model for the three-body interaction potential and the approximations used in deriving the expression for  $k_r^B$  are no longer valid. A more realistic model for the interaction potential must be assumed and a more detailed analysis will be involved in the calculation. Work in this direction is being pursued at this laboratory on the (H + H + H) system which, hopefully, will shed some light on the question as to why, in dissociation and recombination processes, the parent atoms are much more efficient third-body collision partners than those which are "inert."

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## COMMENTS

*K. N. C. Bray, The University, Southampton, England.* I would like to ask some questions about the contributions from electronically excited molecular states, which the calculations show to be important in some cases. The effective recombination rate will then be very sensitive to the electronic population distribution. The assumption of a Maxwellian distribution among these states implies that electronic de-excitation occurs on a much shorter time scale than recombination and vibrational de-excitation through the bottleneck. Presumably, then, molecules formed in electronically excited states must be assumed to undergo rapid transition to the electronic ground state, where they will appear as source terms at various levels in the vibrational energy ladder. Does the Keck and Carrier nonequilibrium correction factor require modification to allow for these source terms? Are there cases where electronic and vibrational characteristic times are comparable, so that the electronic equilibrium assumption fails and the vibrational de-excitation rates of electronically excited states also become important? Finally, is there conceivably any way of increasing the rate of recombination by modifying the populations of electronically excited states?

*Authors' Reply.* In our theoretical development (see Ref. 4 of the paper) we have assumed that electronic transitions do not occur during interactions, so that the complete three-body interaction potential remains invariant in accordance with the Born–Oppenheimer separation. We have thus treated the reaction chemistry of each electronic state as though it were occurring in complete isolation from the other states of the system. Electronic state transitions which occur from vibrational levels in the vicinity of the bottleneck at rates faster than vibrational excitation and de-excitation through the bottleneck could disturb the steady-state vibrational distributions which we have used; i.e., it would be necessary to include additional source terms in the vibrational relaxation master equations, which Keck and Carrier did not do. Unfortunately, experimental measurements on which to base quantitative representations of these source terms are not available. However, by considering the case of recombination, for example, it is clear that any collisional process in which either (a) sufficient electronic energy is transferred to place the recombining molecule in a vibrational level which is below the bottleneck of the new electronic state, or (b) sufficient vibrational energy is transferred from the recombining molecule to stabilize it below the bottleneck, will enhance

the net rate of recombination. For optically thin gases, radiative decay of the excited molecules could also result in an increased recombination rate, although rapid radiative decay of upper electronic molecular states has the effect of decreasing the net dissociation rates which we have calculated.

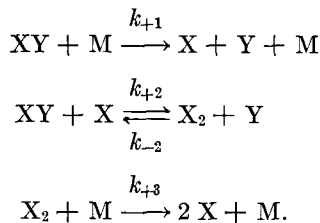
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*S. H. Bauer, Cornell University.* In the discussion of the dissociation of XY, it is not correct to identify

$$\begin{aligned} -(d[XY]/dt)_{\text{exp}} &= (d[X]/dt)_{\text{exp}} \\ &= (d[Y]/dt)_{\text{exp}}, \end{aligned}$$

since there are other paths for the removal of XY besides direct dissociation. Hence, care must be used in comparing your theoretical results with published experimental results. Clearly the analysis of the self-atom collider efficiency will be the crucial test of the theory. I am under the impression that the superposition assumption is not too bad for the three-atom case.

*Authors' Reply.* We agree with Prof. Bauer that the equation relating the disappearance rate of the molecules to the appearance rate of the atoms is not generally valid. However, we have tacitly assumed in our calculations, and in our comparisons with the experimental results, that all intermediate species have achieved steady-state concentrations. Under these circumstances, our equation is valid. For instance, a reaction path for the dissociation of the heteronuclear molecule XY, other than by electronically excited states, could be via the formation of the intermediate X<sub>2</sub> (or Y<sub>2</sub>) according to:



By assuming a steady-state concentration of X<sub>2</sub>, i.e.,

$$\begin{aligned} d[X_2]/dt &= k_{+2}[XY][X] \\ &\quad - k_{-2}[X_2][Y] - k_{+3}[X_2][M] \\ &= 0, \end{aligned}$$

one still obtains:

$$-d[XY]/dt = d[X]/dt = d[Y]/dt.$$

The case of highly reactive third bodies will certainly provide another test of the theory. Work in this direction for three hydrogen atoms is currently in progress, using a fairly realistic potential energy surface, such as that given by Cashion and Herschbach.<sup>1</sup> From a comparison of the results of this study and those obtained by assuming superposition, it should be possible to test the generality of the superposition assumption for three-atom systems.

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*J. Troe, Universitaet Goettingen, Germany.* It has been shown earlier that rate constants of this kind may be rationalized in terms of statistical quantities like the total cross section for energy transfer, the mean-squared energy transferred per collision, and sometimes also the mean absolute value of energy transferred per collision. Can you extract these quantities from your calculations and, more especially, can you comment on the temperature dependencies, the absolute values of the energy averages compared to  $kT$ , and the dependencies of these quantities on the energy content of the molecules before collision?

*Authors' Reply.* The quantities referred to by Dr. Troe can, in principle, be obtained by statistical sampling of the phase-space trajectories which cross the "barrier surface." However, this information was not compiled in the particular trajectory calculations which were used in this study (see Refs. 1 and 18 of the text).