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DURATION OF ATOMIC COLLISIONS:
A NOTE ON RECOMBINATION RATE THEORY

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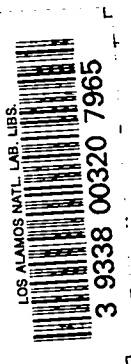
DURATION OF ATOMIC COLLISIONS:
A NOTE ON RECOMBINATION RATE THEORY

By

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ABSTRACT

A mechanical treatment of atomic recombination reactions is developed for the case in which the reaction is considered to involve an intermediate excited molecule which is stabilized on collision with any third body. An explicit rate calculation is given for the reaction $I + I + A \rightarrow I_2 + A$. The results of this are compared with those obtained by treating other models of recombination. The validity of the excited intermediate model and the role of electronic degeneracy are discussed.



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INTRODUCTION

The calculation described in this report arises in the study of atomic recombination rates. The over-all reaction will be written



in which M is any gaseous third body. Whenever an attempt is made to relate the mechanical details of reaction (1) to the observed properties of recombination rates,^{1,2} the simple mechanism



immediately suggests itself for study. X_2^* is a "collision complex" with a definite lifetime τ , and it is supposed that a net recombination reaction occurs if this complex collides during its lifetime with a third object M, transferring to it (with a certain probability P) enough energy so that the molecule X_2 cannot subsequently dissociate. The third-order rate constant k_R for recombination is defined by

$$\frac{d[X_2]}{dt} = k_R [X]^2 M;$$

$$k_R = P Z_a Z_b \tau \equiv P Z_b K. \quad (3)$$

Z_a and Z_b are collision numbers for reactions (2). If τ is independent of temperature (for example, taken as the harmonic vibration period of X_2), it is not possible to make a consistent set of assumptions about P which will account for the experimental evidence in terms of reactions (2). This method of estimating τ has been criticized for failing to consider collisions with appreciable angular momentum and for assuming that energy transfer can occur only when the colliding atoms are interacting along the harmonic part of their potential curve.

Recently Keck³ has proposed a theory which can be used, in effect, to calculate an upper limit to the product PK . His treatment replaces consideration of the mechanical details of collisions with certain a priori statements (which will be discussed in detail later) about the statistics of the three-body process. He has applied this theory to the case $X = \text{iodine}$, $M = \text{argon}$.

This report gives the results of an adequately precise calculation, based on mechanics, of the product $Z_b K$ for the same case. The k_R obtained from this calculation will be compared with that derived from the Keck theory, and also with predictions arising from the

alternate mechanisms which invoke the reactions $X + M \rightleftharpoons XM^*$. This comparison allows some discussion to be given of the relative plausibility of the various theoretical approaches to recombination kinetics.

THE RADIAL EQUATION OF MOTION

The Lagrangian function for two particles colliding in the center-of-mass system is

$$L = \frac{1}{2} \mu (\dot{r}^2 + r^2 \dot{\theta}^2) - V. \quad (4)$$

μ is the reduced mass of the particles, r their separation, and θ the angular coordinate about the center of mass; V is an as yet unspecified central interaction potential which will be defined so that $V = 0$ corresponds to dissociation. The derived differential equation in r is

$$\mu \ddot{r} - \mu r \dot{\theta}^2 + \frac{dV}{dr} = 0. \quad (5)$$

The angular momentum, $M = \mu r^2 \dot{\theta}$, is to be expressed in terms of the familiar impact parameter $b = M/\mu v$, where v is the relative velocity of the particles at large r . Equation (5) can then be rewritten in terms of b and of incident kinetic energy $E = \frac{1}{2} \mu v^2$:

$$\mu \ddot{r} - \frac{2Eb^2}{r^3} + \frac{dV}{dr} = 0, \quad (6)$$

and one integration may be performed at once. The result is

$$\frac{2E}{r^2} = E \left(1 - \frac{b^2}{r^2} \right) - V. \quad (7)$$

This equation describes the behavior of the separation coordinate r during a collision fully specified by values of the two parameters: E , the kinetic energy at large r ; and b , the closest distance at which the particles would pass if there were no interaction between them.

We are particularly interested in the time required to cover a certain range of r . It is

$$t = \left(\frac{2E}{r^2} \right)^{\frac{1}{2}} \int_{r_1}^{r_2} \left[E \left(1 - \frac{b^2}{r^2} \right) - V \right]^{-\frac{1}{2}} dr. \quad (8)$$

b_{\max} ; THE ROTATION BARRIER

Consider an attractive potential which at large r dies away according to a power law $V = -Ar^{-n}$. It is evident that for certain values of E , b , r , n , and A , the integrand in Eq. (8) may be imaginary. As an example for discussion suppose that $V = -4\epsilon_0(\sigma/r)^6$, which is the attractive part of a Lennard-Jones potential;

$$\text{Integrand} = \left[E \left(1 - \frac{b^2}{r^2} \right) + 4\epsilon_0(\sigma/r)^6 \right]^{-\frac{1}{2}}. \quad (9)$$

If E is specified in (9), a sufficiently small b will allow the integrand to be always real, and the particles may approach to any r , however small. On the other hand, if b is large, there will be a range of r in which the integrand is imaginary, and the particles will be unable to cross it. This is the way in which the "rotation barrier" appears in this formulation. Obviously there is a critical b , which will be called b_{\max} ; only collisions with $b < b_{\max}$ will involve a crossing of the rotation barrier.*

For this potential it is easy to find b_{\max} , by setting the bracket in (9) and its first derivative simultaneously equal to zero. The result is

$$r_{\max} = 2^{\frac{1}{2}} \sigma \left(\frac{\epsilon_0}{E} \right)^{\frac{1}{6}} ; \quad b_{\max} = \left(\frac{3}{2} \right)^{\frac{1}{2}} r_{\max} . \quad (10)$$

We expect the inverse r^6 potential to be fairly realistic in the vicinity of r_{\max} (the interaction energy there is $-V = \frac{1}{2} E$), so a more elaborate potential function should lead to values of r_{\max} and b_{\max} not very different from the above.

We propose to define the duration of the collision as the time during which the particles are inside the rotation barrier. The r at which the barrier occurs gradually becomes greater as b is

* For other treatments in which the rotation barrier is defined in this way and in which related integrals arise, see e.g., D. E. Stogryn and J. O. Hirschfelder, University of Wisconsin Report WIS-ONR-32, March 15, 1958; and M. A. Eliason, D. E. Stogryn, and J. O. Hirschfelder, Proc. Nat. Acad. Sci. 42, 546 (1956).

decreased below b_{\max} ; it is infinite for $b = 0$. We will therefore at first assume that V must be cut off at some large value of r in order to prevent interactions at absurdly great distances; later it will be shown that this is unnecessary.

The quantity we wish eventually to calculate is K , the equilibrium constant of Eq. (3). This is given by

$$K = \int_0^{\infty} \int_0^{b_{\max}} Z(E,b) \tau(E,b) db dE; \quad (11)$$

it is an average over suitably weighted and normalized distributions of b and E . $Z(E,b) = (2b/b_{\max}^2) Z(b_{\max})n(E)$. $Z(b_{\max})$ is a collision number with the cross section term replaced by b_{\max}^2 ; then

$(2b/b_{\max}^2)Z(b_{\max})db$ is the absolute rate of collisions with the impact parameter between b and $b + db$. $n(E)dE$, with $n(E)$ a normalized Boltzmann distribution, gives the fraction of these with energy between E and $E + dE$. Equation (11) can, for convenience, be rewritten

$$K = \int_0^{\infty} Z(b_{\max})n(E)\tau(E)dE, \quad (12)$$

where, from Eq. (8),

$$\tau(E) = \frac{2}{b_{\max}^2} \left(\frac{\mu}{2}\right)^{\frac{1}{2}} \int_0^{b_{\max}} b \int_0^{\infty} \left[E \left(1 - \frac{b^2}{r^2} \right) - V \right]^{-\frac{1}{2}} dr db. \quad (13)$$

The \int is to cover the trajectory of the particles between the times the rotation barrier is crossed, first in the inward and then the outward direction. $\tau(E)$ is the average collision duration for a particular incident kinetic energy. We can calculate it, and thus K , if V is known.

THE POTENTIAL FUNCTION

It is instructive, as a first approximation, to allow V to be the inverse r^6 potential given in Eq. (9). We cut off the integration at the arbitrary values $\rho < r_{\max}$ and $\rho' > r_{\max}$. The location of the rotation barrier is at $r = (3/2)^{1/2} r_{\max}^{3/2} / b^{1/2}$. It is easiest to integrate first over b .

$$\tau(E) = \left(\frac{\mu}{2E}\right)^{1/2} \frac{4}{b_{\max}^2} \left[\int_{\rho}^{r_{\max}} \int_0^{3/2 r_{\max}} \frac{b \, dr \, db}{\sqrt{1 - \frac{b^2}{r^2} + \frac{1}{2} \frac{r_{\max}^6}{r^6}}} + \int_{r_{\max}}^{\rho'} \int_0^{3/2 \frac{r_{\max}^3}{r^2}} \text{same integrand} \right]. \quad (14)$$

After the b integration is performed, the substitutions $u = (r/r_{\max})^2$, $\alpha = (\rho/r_{\max})$, $\alpha' = (\rho'/r_{\max})$ are made. The result is

$$\tau(E) = \left(\frac{\mu}{2E}\right)^{\frac{1}{2}} \frac{4}{3} r_{\max} \left[\int_{\alpha^2}^{\alpha'^2} \frac{(u^3 + \frac{1}{2})^{\frac{1}{2}}}{u} du - \int_{\alpha^2}^1 \frac{(u^3 - \frac{3}{2}u^2 + \frac{1}{2})^{\frac{1}{2}}}{u} du - \int_1^{\alpha'^2} \frac{(u^3 - 1)^{\frac{1}{2}}}{u} du \right]. \quad (15)$$

The bracket in Eq. (15) was evaluated* as a function of the limits α and α' . It was found to approach a constant value rapidly as α became small or α' large. The points at which it had one-half the value obtained for $(\alpha = 0, \alpha' = \infty)$ were: $\alpha = 0.85, \alpha' = 1.24$. Thus, it is a fair approximation to adopt the limits $(0, \infty)$, in which case

$$\tau(E) = 1.500 \left(\frac{\mu}{2E}\right)^{\frac{1}{2}} r_{\max} = \frac{3}{2} \sigma \mu^{\frac{1}{2}} \epsilon_0^{\frac{1}{6}} E^{-\frac{2}{3}}. \quad (16)$$

The integration over the Boltzmann distribution, Eq. (12), may now be performed, and the result is

$$K = 18\sqrt{2\pi} \sigma^3 \sqrt{\frac{\epsilon_0}{kT}}. \quad (17)$$

*This calculation and others which follow were performed with the aid of an IBM 704 computer. Portions of the problem coded with FORTRAN were checked by graphical integration or hand calculation; portions coded by ordinary means were either made self-checking or tested by graphical methods.

Thus, in this approximation, the calculated rate constant $k_R = KZ_b$ will be independent of temperature. It will also be too large because the r^{-6} potential is nearly zero over too large a range of r to be correct in (high energy) cases where r_{max} is small. It was decided, on the basis of this preliminary calculation, that a sufficiently accurate result -- i.e., within a factor of 2 -- could be obtained by using a "realistic" potential, carrying out the above integration between the rotation barrier and the turning point, and allowing $r \rightarrow \infty$ as before.* Because neither the r^{-6} potential nor the Morse function adequately represents the interaction at intermediate distances, it was necessary to invent a mathematical representation which resembles the former at large r and the latter at small r , with a smooth transition between the two. Since the rotation barrier (where the largest contribution to τ arises) and the transition region (where the Morse function and the inverse power potential are equally inaccurate) occur near the same value of r , a fairly refined potential function is required if the desired precision in τ is to be obtained.

The potential function used was

* In practice, the calculation was simplified (with negligible effect on the results) by cutting off the range of r at 9 Å and integrating from the bottom of the potential well to the rotation barrier.

$$V = \alpha D_e \left\{ e^{-2\beta(r - r_e)} - \frac{2e^{-\beta(r - r_e)}}{[1 + (r - r_e)^2]^n} \right\} + 4\epsilon'_0 \left[\left(\frac{\sigma'}{r} \right)^m - \left(\frac{\sigma'}{r} \right)^6 \right]. \quad (18)$$

In this expression, the first term is an ordinary Morse function, multiplied by a constant (α) and with its attractive term divided by a quantity which makes it approach zero more rapidly. The second term is a modified Lennard-Jones potential. Three conditions are needed to determine ϵ'_0 , σ' , and m . In this case these were:

(1) that the modified Lennard-Jones potential be zero when the Morse function is; thus the resulting potential would also be zero at this point; (2) that the minima of the first and second terms be at the same r ($= r_e$), so the resulting minimum is not shifted; (3) that the modified Lennard-Jones potential have the correct coefficient of r^{-6} at large r ; that is, $\epsilon'_0 \sigma'^6 = \epsilon_0 \sigma^6$, where ϵ_0 and σ are the potential parameters used in the preliminary, approximate calculation.

The above conditions being met, the constant α is adjusted until the minimum of the curve corresponds to the correct dissociation energy D_e . This leaves to be determined the quantity n , which is found to govern the separation at which the transition from Morse to r^{-6} behavior occurs. n was determined by a modification of the semi-classical method of Klein and Rydberg.⁴ For $X_2 = I_2$, the case of interest, there are known⁵ three anharmonicity constants, referring

to the spacing of vibrational levels (so in principle we can know the potential much better than it is given by the Morse curve, which takes account of only one anharmonicity term). The energy of the 50th vibrational level can be calculated from these with fair accuracy. n is chosen so that

$$\oint [2\mu(E_{50} - V)]^{\frac{1}{2}} dr = 50.5h, \quad (19)$$

where the integration extends over one cycle of motion; that is, the volume of phase space defined by V and the 50th level must be able to contain just $50\frac{1}{2}$ quantum states.

For I_2 , if we take $\epsilon_0^I = \epsilon_0^{Xe}$ and $\sigma^I = \sigma^{Xe}$, we may use the parameters $m = 9$, $n = 1$, $\alpha = 0.784$, $\sigma' = 2.29 \text{ \AA}$, and $\epsilon' = 0.573 \text{ e.v.}$ A closer fit ($n = 1.1$) was found, but the foregoing are sufficiently accurate for this calculation.

The integrations over r , b , and E , already described, were repeated using the potential function given above, for a series of temperatures. The rate constant $k_R = PZ_b K$ was calculated vs T , using $P = 1$, and for the cross section term in Z_b , $\frac{1}{4}(\sigma_M + \bar{r}_{\max})^2$, where \bar{r}_{\max} is the r_{\max} for $E = kT$. The results, which are intended to represent an exact (for kinetics purposes) calculation of k_R if $P = 1$, and the mechanism is given by reactions (2), were obtained in tabular form and will be discussed in the next section.

DISCUSSION

The information obtained from the foregoing calculation is to be compared with the predictions of the Keck theory.³ We first seek to establish the relationship between our treatment and that of Keck.

Keck assumes that a three-body collision is sufficiently complicated that the internal states of the three-body complex become populated in an equilibrium fashion and the mechanical details of the formation of the complex may therefore be ignored. In statistical language, this is to say that the density of representative points leaving the region of phase space which corresponds to the three-body complex is uniform. Aside from its other merits, this assumption requires that the transition probabilities for internal-translational energy exchange be large; if this is not entirely true, Keck's calculated rate should exceed the rate which is observed. He also assumes, in applying the theory to the reaction $I + I + A \rightarrow I_2 + A$, that the I-I interaction is given by a Morse function (cut off at $-V = kT$) and that I and A interact as rigid spheres. This has the effect of a restriction that the recombination shall occur via the mechanism given in reactions (2).

Keck, then, obtains an expression for k_R which is an upper limit to the observed rate, and our calculation is in turn an upper limit to Keck's. The experimental data should be less than his calculated results to the extent that the contribution to P arising from

quantum-mechanical transition probabilities is less than unity; his calculation should give smaller answers than ours to the extent that the purely geometric and mechanical part of P is not unity, since his theory takes account of this latter and our calculation does not.

It can be seen from Fig. 1, which displays the observed rates,⁷ our results, and those of Keck (without the electronic degeneracy factor; see later), that these predictions are correct. Further support for Keck's postulates can be obtained from the fact that, for $kT \ll D_e$ (classified by Keck as the condition for applicability of the so-called "three-body collision" theories), his results reduce to a form very similar to ours. Thus the assumption that the mechanics of the three-body collision may be ignored seems to be verified, at least for the case of $X = I$ and $M =$ noble gas, with mechanism (2) operating at reasonably low temperatures. That the three curves diverge at high temperature is to be expected, since the probability factors should decrease as the temperature is raised.

A conclusion can be drawn from our results which has not yet been obtained from the Keck theory. The value of P for argon is sufficiently small that, assuming $P \sim 1$ for complicated M , it is at least possible that the mechanism (2) could account for the observed variation of k_R with M . The simple mechanical treatment of this mechanism, mentioned in the introduction, was open to the fatal objection² that it required $P \sim 1$ for argon. To account for the

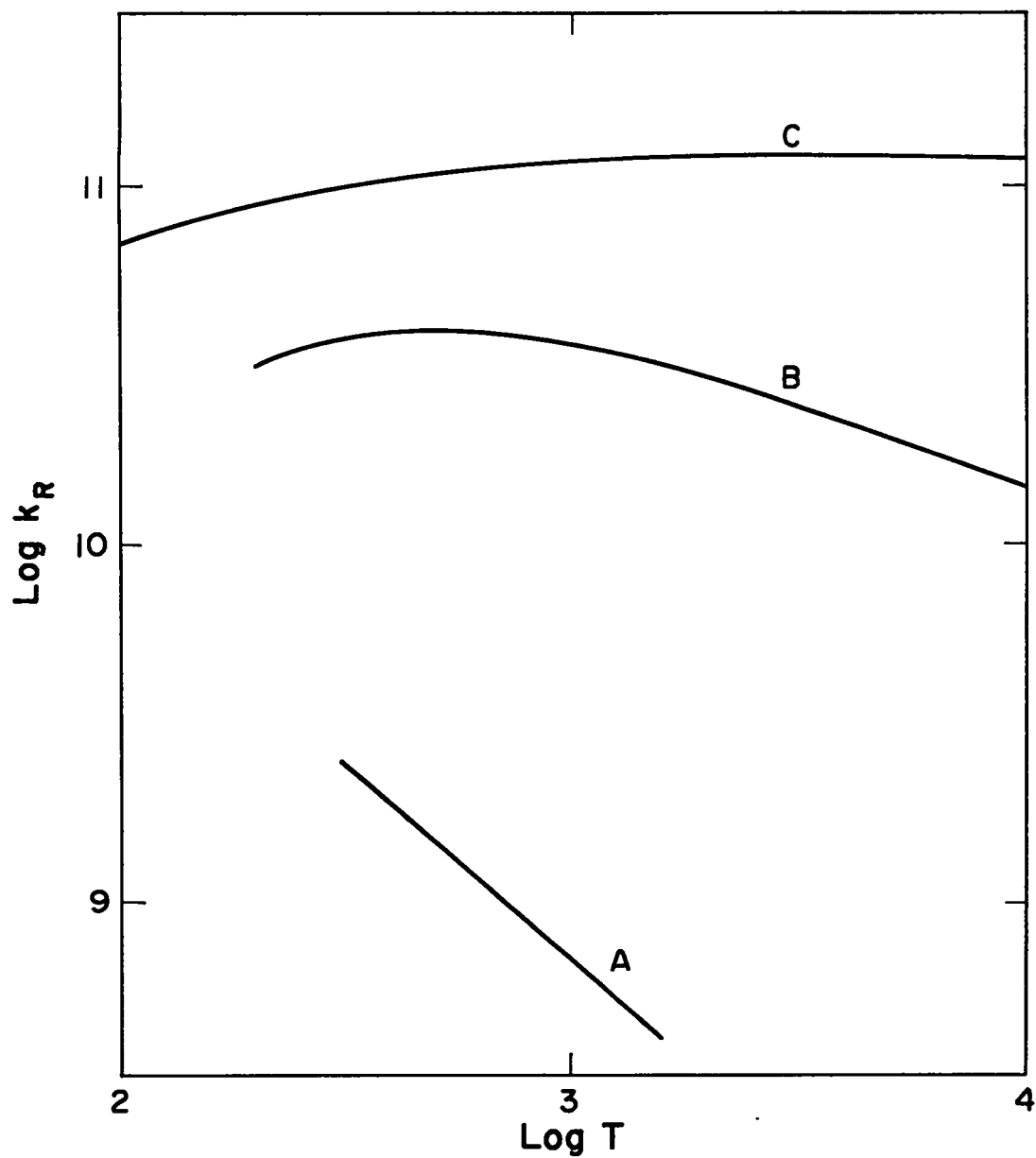


Fig. 1. $\text{Log } k_R$ ($\text{l}^2 \text{mole}^{-2} \text{sec}^{-1}$) vs $\text{log } T$ ($^{\circ}\text{K}$) for $\text{I} + \text{I} + \text{A} \rightarrow \text{I}_2 + \text{A}$.
 Curve A: Observed rate constant. Curve B: Keck Theory.
 Curve C: Mechanical calculation of K. Curves B and C do not contain correction for electronic degeneracy (see text).

behavior of polyatomic M, it was necessary to take $P \sim 10$ in some cases, which is absurd. This objection is now removed; by suitable variation of P with the nature (and also the mass) of M, and with temperature, the mechanism (2) could account for most of the observed features of recombination reactions.

The alternate mechanism



has also been shown² to lead to predictions in substantial accord with the observations. The requirement for a successful theory based on this mechanism is that for any M, $P \sim 1$ for the process $XM_{eq} + X \rightarrow X_2 + M$ (where XM_{eq} is the equilibrium population of XM in bound states) and that $P \ll 1$ for all other processes leading to recombination, including reaction (2b) of this report. Thus, there exist two independent theoretical approaches, derived from contradictory sets of postulates, each of which is at least capable of explaining the observed behavior of recombination reactions, and between which an unequivocal choice cannot at present be made.

There remains one further complication to be discussed. Keck introduces into P an additional factor of $1/16$, which may be called the electronic degeneracy factor. It arises because each of the two ground state ($^2P_{3/2}$) iodine atoms has its lowest energy level split

into four components by interaction with the other. Of the resulting 16 possible combinations only one leads to the $^1\Sigma$ ground state of I_2 , so that if no electronic transitions occur, only one of 16 collisions can lead to recombination.

It has, however, been pointed out that there are other known molecular states of I_2 which range from slightly to markedly attractive. The total degeneracy of these plus the ground state is at least 5. It might also be added that the calculation described in this report indicates that the largest contribution to recombination comes from $b \sim b_{\max}$, so that the "effective" potential for all states possesses a considerable rotation barrier. It is possible that the molecule might be deactivated into one of these metastable states and reach the $^1\Sigma$ state by subsequent processes.

These arguments, for and against the $1/16$ electronic degeneracy factor, appeared in the literature⁸ of the late 1930's, and no new conclusion about the validity of this factor appears possible at the present time. However, the effect of its inclusion in the theories discussed above should be noted.

If the electronic degeneracy factor is as small as about $1/5$, the theory based on mechanism (20) is certainly invalid. A factor of $1/16$ brings the Keck theory into reasonable agreement with observation for the case $X = I$, $M = A$ (and other noble gases). However, on the basis of the calculation described here, if this factor is

small, the ability of mechanism (2) to account for the high efficiency of polyatomic M in promoting recombination is lost because there is no longer sufficient margin between theory and observation to allow P to vary in the required way.

SUMMARY

A detailed mechanical calculation of the equilibrium constant K for the reaction $2\text{I}({}^2\text{P}_{3/2}) \rightleftharpoons \text{I}_2^*({}^1\Sigma)$ has been made. The results, as applied to recombination reactions, are consistent with the statistical theory of Keck, and with the experimental observations provided (in the latter case) that the probability factor associated with electronic degeneracy is not too small. Since the results of this calculation indicate that no existing theory will completely account for the known properties of recombination rates unless electronic transitions are allowed (i.e., electronic degeneracy factor $>1/16$), a decision cannot at present be made as to the relative merits of the two bimolecular mechanisms which have been proposed for recombination reactions.

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