

Rate Constants for the Process $\text{O}_2 + \text{ArO} + \text{O} + \text{Ar}$

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Citation: *The Journal of Chemical Physics* **45**, 1078 (1966); doi: 10.1063/1.1727673

View online: <http://dx.doi.org/10.1063/1.1727673>

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measurements to $(\Delta P)^2 \sim 0.02$ at the excitation energy of 500 V. The scattered current for the 2^1S and 2^1P peaks in helium which are well resolved in all spectra, was measured at several scattering angles from $\theta = 0.5^\circ$ to $\theta = 2.5^\circ$. Zero-angle data were excluded because of an uncertainty in the scattering angle due to slit length. The cross section for the 1^1S - 2^1S transition was calculated from the experimental intensity ratios at each scattering angle using a calculated cross section for the 1^1S - 2^1P transition.⁸ Equation (1) was then used to calculate the generalized oscillator strength $f(2^1S)$. The results are given in Fig. 1, and a straight-line extrapolation would yield a small but finite limiting value of $f(2^1S)$. Nevertheless, it has been shown⁹ that selection rules apply to excitation by electron impact and the limit of the generalized oscillator strength is the same in the first and second Born approximations, and f_2^1S should extrapolate to zero.

In a recent paper¹⁰ Lassettre has discussed a power series expansion that represents the generalized oscillator strength for the 1^1S - 2^1S transition and has used this series to fit the experimental data of previous investigations. We have applied this method [Eqs. (36) and (37) of Ref. 10] to the data of the present research and obtained a curve that agrees with the measured points within the limits of experimental error (see the solid line in Fig. 1). It is of some interest to note that a curve instead of a straight line is obtained by this method, and the limiting slope, $f/(\Delta P)^2$ is 0.099 as $(\Delta P)^2 \rightarrow 0$. The value of this slope fitting the earlier data [$(\Delta P)^2 > 0.18$] to Eq. (36), Ref. 10 is 0.092 and fitting the same data to Eq. (39), Ref. 10 $\lim f/(\Delta P)^2 = 0.089$. An independent extrapolation of the same data by Garstang⁵ yields a limiting value of 0.09 ± 0.02 . Considering that a different, higher-resolution spectrometer has been used in this work and measurements have been made at smaller values of $(\Delta P)^2$ the agreement between the two sets of data is quite good.

Garstang⁵ has also calculated the reduced matrix element of the electric quadrupole moment and obtained $\lim f/(\Delta P)^2 = 0.13$. Our results show much better agreement with this value than with the limiting slope derived by Garstang⁵ from the calculations of Altshuler.¹¹

* Supported in part by the U.S. Air Force Office of Scientific Research under Grant No. AF-AFOSR-61-63.

¹ E. N. Lassettre, *Radiation Res. Suppl.* **1**, 530 (1959).

² E. N. Lassettre and S. A. Francis, *J. Chem. Phys.* **40**, 1208 (1964).

³ E. N. Lassettre and M. E. Krasnow, *J. Chem. Phys.* **40**, 1248 (1964).

⁴ E. N. Lassettre, V. D. Meyer, and M. S. Longmire, *J. Chem. Phys.* **41**, 2952 (1964).

⁵ R. H. Garstang, *J. Chem. Phys.* **44**, 1308 (1966).

⁶ E. N. Lassettre, M. E. Krasnow, and S. M. Silverman, *J. Chem. Phys.* **40**, 1242 (1964); S. M. Silverman and E. N. Lassettre, *ibid.* **40**, 1265 (1964).

⁷ V. D. Meyer, A. Skerbele, and E. N. Lassettre, *J. Chem. Phys.* **43**, 805 (1965).

⁸ E. N. Lassettre and E. A. Jones, *J. Chem. Phys.* **40**, 1218 (1964).

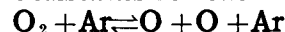
⁹ E. N. Lassettre, *J. Chem. Phys.* **42**, 2971 (1965).

¹⁰ E. N. Lassettre, *J. Chem. Phys.* **43**, 4479 (1965).

¹¹ S. Altshuler, *Phys. Rev.* **89**, 1093 (1953).

Comments

Rate Constants for the Process



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THERMAL dissociation of diatomic molecules is a multistep process involving gradual transition of the dissociating molecule to increasingly higher vibrational levels up to that of dissociation. Nikitin¹ has shown that in order to allow for the above, a factor $\delta E/kT$ accounting for dissociation-induced violation of equilibrium distribution of vibrational energy over higher energy levels should be introduced into the formula for k_d

$$k_d = C(T)^{\frac{1}{2}} (\delta E/kT) [1 - \exp(-h\omega/kT)] \exp(-D/kT)$$

[Eq. (17.10) in Nikitin's book]. The factor $\delta E/kT$ arises from the product $\langle \Delta E^2 \rangle_{g_{\text{vib}}} / (kT)^2$ the first factor of which represents the coefficient for diffusion over energy levels, and the second is the number of vibrational states in the kT energy range in the equilibrium-violation zone. For a one-quantum excitation model the mean square of the energy transferred $\langle \Delta E^2 \rangle$ is equal, by an order of magnitude, to the square of one vibrational quantum δE at an energy $E^* \simeq D - kT$. On the other hand, we have $g_{\text{vib}} \simeq kT/\delta E$, so that ultimately $\langle \Delta E^2 \rangle_{g_{\text{vib}}} / (kT)^2 \simeq \delta E/kT$. Neglecting the temperature dependence of the vibrational and electronic statistical weights and assuming that $\delta E \sim T^{\frac{1}{2}}$,¹ we obtain

$$k_d = C' [1 - \exp(-h\omega/kT)] \exp(-D/RT),$$

which becomes

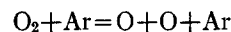
$$k_d = C'' T^{-1} \exp(-D/RT)$$

for high temperatures and

$$k_d = C' \exp(-D/RT)$$

for low temperatures.

The most accurate determinations of the rate constant for the thermal dissociation of oxygen by the scheme



seem to be those made by Wray,^{2,3} who obtained, by using the shock wave method, the formula

$$k_d = 2.5 (\pm 14\%) \times 10^{16} T^{-\frac{1}{2}}$$

$$\times \exp(-D/kT) \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1}$$

valid for the temperature range of 5000°–18 000°K. However, Wray does not discard the formula with the pre-exponential factor containing T^{-1} (Ref. 3, p. 527).

Moreover, in Ref. 2 (footnote to p. 1523) he gives a formula,

$$k_d = 2.4(\pm 18\%) \times 10^{18} T^{-1} \\ \times \exp(-D/RT) \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1},$$

that shows almost the same agreement with experiment, and is consistent with the above theoretical formula with respect to the pre-exponential temperature dependence.

A form valid for any temperature is

$$k_d = 1.1 \times 10^{18} [1 - \exp(-2200/T)] \\ \times \exp(-D/RT) \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1}.$$

The recombination constant k_r may be obtained from this formula and those given in Ref. 3 for the equilibrium constant $\text{O}_2 \rightleftharpoons 2\text{O}$, on the basis of relation

$$K = k_d/k_r$$

the validity of which was established in this paper. The rate constant thus calculated is $k_r = 3.5 \times 10^{13} \text{ cm}^6 \text{ mole}^{-2} \cdot \text{sec}^{-1}$ at 2000°K , compared to that given by Wray $k_r = 2.5 \times 10^{13}$, and $k_r = 1.4 \times 10^{14} \text{ cm}^6 \text{ mole}^{-2} \cdot \text{sec}^{-1}$ at 300°K compared to the upper limit of this constant $k_r < 3.2 \times 10^{14}$ obtained by Morgan and Schiff.⁴

The general expressions for recombination rate constants may be written as

$$k_r = 4.2 \times 10^{16} T^{-1} \text{ cm}^6 \text{ mole}^{-2} \cdot \text{sec}^{-1}$$

for close to room temperatures and

$$k_r = 2.0 \times 10^{15} T^{-3} \text{ cm}^6 \text{ mole}^{-2} \cdot \text{sec}^{-1}$$

for temperatures higher than 3000°K .

¹ E. E. Nikitin, *Theory of Thermally Induced Gas Phase Reactions* (Indiana University Press, Bloomington, Ind., 1966).

² K. L. Wray, *J. Chem. Phys.* **38**, 1518 (1963).

³ K. L. Wray, *Symp. Combust.* 10th Cambridge Univ., Cambridge, England, 1964, 523 (1965).

⁴ J. E. Morgan and H. I. Schiff, *J. Chem. Phys.* **38**, 1495 (1963).

Diffusion Along Dislocations*

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(Received 23 February 1966)

WE would like to make the following comments concerning the recent interesting paper¹ with the above title by Luther, in which the effect of a dislocation on diffusion is taken into account by assuming a volume diffusion coefficient inversely proportional to the square of the radial distance from the dislocation.

(1) The author points out that his hypothesis does not require any assumption of a more-or-less arbitrary radius for a dislocation "pipe." It should be recognized, however, that the choice of exponent in the expression $D = D_0 r^{-n}$ for the diffusion coefficient is equally arbitrary and, according to the calculations presented in Luther's

paper, not readily determined from experiment. To render this model [or a similar one based on Luther's Eq. (4)] more realistic, one would have to introduce an outer cutoff radius as well, beyond which the diffusion coefficient would have its bulk value. As for the diffusion profile near the surface, this can be determined in the pipe model without any trouble in principle, although the calculations are somewhat complex. It would seem to be somewhat easier to separate "volume" and "dislocation" effects in a pipe model, but one of the points of Luther's paper is that such a separation is somewhat illusory.

(2) It is not clear to us how the boundary conditions used by Luther relate to possible experimental conditions. The surface concentration is taken to be independent of r and turns out to vary with time as $t^{-3/4}$. The logarithm of the concentration appears to vary linearly with the distance from the surface. If, as seems to be implied, the boundary conditions are supposed to be those of an "instantaneous" (thin-film) source, it is somewhat surprising that the solution far from the dislocation is not more similar to that for pure volume diffusion from a thin source. Furthermore, it appears that the concentration vanishes at $r=0$, where the diffusivity is greatest. It is entirely possible to treat this model with the conventional constant-source or instantaneous-source boundary conditions by straightforward integral-transform techniques, but we have not so far succeeded in obtaining solutions except in the form of complicated multiple integrals.

(3) The inverse Laplace transform obtained in Appendix B of Luther's paper is incorrect. The particular transform in question, $\mathcal{L}^{-1}[p^{-3/4} \exp(-\gamma p^{1/4})]$ was found by Humbert² to be $-\frac{1}{2}(\pi/2t)^{1/2} H_{1/2,1/4}(3\gamma^{4/3}/4^{4/3}t^{1/3})$, where $H_{m,n}(x)$ is what might be called a Hankel function of two subscripts and is related to hypergeometric series of the type ${}_0F_2$. (See Humbert or McLachlan *et al.*³ for details.) Alternatively, the transform may be expressed in terms of a Meijer G function,⁴

$$\mathcal{L}^{-1}[p^{-3/4} \exp(-\gamma p^{1/4})] \\ = \left(\frac{4}{\gamma}\right)^{15/4} (2\pi^3)^{-1/2} G \left[\begin{matrix} 40 \\ 14 \end{matrix} \left[\begin{matrix} (\frac{1}{4}\gamma)^{4/3} t^{-1} \\ \frac{5}{4}, \frac{3}{4}, \frac{5}{4}, \frac{3}{4} \end{matrix} \right] \right].$$

Luther's result gives the first two terms of an asymptotic expansion correctly and is thus a good approximation for large t or small γ .

For small t we find that

$$\mathcal{L}^{-1}[p^{-3/4} \exp(-\gamma p^{1/4})] \sim t^{-1/6} \exp[-3(\gamma/4)^{4/3} t^{-1/3}],$$

which is in striking disagreement with Luther's Eq. (B11). The error in Luther's analysis stems from assuming that the particular solution to (B5), given in (B6), is the general solution to that equation.

* Work supported in part by U.S. Air Force Office of Scientific Research Grant AF-AFOSR-262-63.

¹ L. C. Luther, *J. Chem. Phys.* **43**, 2213 (1965).