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Interferometric Measurement in the Shock Tube of the Dissociation Rate of Oxygen†

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The dissociation of oxygen has been observed behind shock waves at Mach numbers of 8 to 10, over a temperature range of 3000–5000°K. Photographs of the shocks were made using a Mach-Zehnder interferometer and a spark light source of effective duration 0.1 μsec. The velocity of the shock was measured using thin-film resistance thermometers to detect its passage. From this velocity and the state of the gas ahead of the shock, one can calculate the state of the gas behind the shock, both in the reaction zone and at equilibrium, from the interferometrically observed density ratios. Up to 12% equilibrium dissociation was obtained, following reaction zones of the order of 1 cm in length. The following rate constant, obtained from classical collision theory for the principal reaction

$$O_2 + O_2 \overset{k_D}{\rightleftharpoons} 2O + O_2,$$
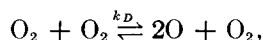
fitted the data well: $k_D = 7.4 \times 10^{11} PT^{\frac{1}{4}}(59\,380/T)^3 \exp(-59\,380/T)$ cc mole^{-1} sec^{-1}, where 59 380 is the known dissociation energy of oxygen, expressed in degrees Kelvin. The quantity P, the "collision efficiency," was adjusted to fit the data, and was found to be 0.07. The data are consistent with the results of several other investigators who used different methods. The recombination rate constant calculated from the dissociation rate constant is 8.4×10^{14} cc^2 mole^{-2} sec^{-1} at 3500°, and is approximately proportional to T^{-2}.

I. INTRODUCTION

THE SHOCK tube is being used more and more in the investigation of gaseous reactions, chemical and otherwise. It can produce temperatures from 400°K to an upper limit as yet undertermined, but high enough to cause not only chemical reaction but multiple ionization. Reaction times from much less than 1 μsec up to about 1 msec can be observed.

The shock tube has been used to observe the approach to equilibrium of rotation,[1] vibration,[2-5] and dissociation[6-13] in diatomic gases, and also in polyatomic gases. A wide variety of techniques has been employed to observe the density of the gas or the concentration of one of the reacting species, e.g., schlieren (a semiquantitative method)[6] and

selective absorption of radiation.[8,10-13] Interferometric studies on oxygen other than this one have been those of Blackman[5] on vibrational relaxation, Byron[7] on dissociation relaxation, and Alpher and White[14] on equilibrium dissociation. Eckerman's[9] work on dissociation relaxation consisted of observing the detachment distance of the bow shock on spheres moving at high velocity through the gas.

II. OUTLINE OF THE METHOD

A shock wave is propagated into oxygen at known temperature and pressure. Such a shock heats the oxygen sufficiently to cause dissociation, and the heating is rapid compared with the rate of dissociation. An "instantaneous" interferogram of the shock and the flow behind it is made using a spark light source of short duration. The fringe shift between any two points on such an interferogram is proportional to the difference in density between the two points. A large and practically discontinuous increase in density marks the position of the shock front, and is followed by a somewhat smaller monotonic increase through the reaction zone, as shown in Fig. 1. The latter density increase arises from the drop in temperature owing to the heat absorbed in the reaction. The experimental conditions are chosen so that the reaction zone is from 1 mm to a few cm in length, and in this zone the density is observed as a function of distance behind the shock.

This experimental result can be compared with

† This work was supported in part by the Office of Naval Research.
[1] D. F. Hornig, J. Phys. Chem. **61**, 856 (1957).
[2] W. Griffith, Phys. Rev. **87**, 234 (A) (1952).
[3] Smiley, Winkler, and Slawsky, J. Chem. Phys. **20**, 923 (1952).
[4] Griffith, Brickl, and Blackman, Phys Rev. **102**, 1209 (1956).
[5] V. H. Blackman, J. Fluid Mech. 1, 61 (1956).
[6] H. S. Glick and W. H. Wurster, J. Chem. Phys. **27**, 1224 (1957).
[7] Stanley Byron, Ph.D. thesis, Cornell University, Ithaca, New York, 1958.
[8] Camac, Camm, Feldman, Keck, and Petty, Preprint 802, Institute of the Aeronautical Sciences, New York, 1958.
[9] J. Eckerman, Ph.D. thesis, Catholic University, Washington, D. C., 1958.
[10] John P. Chesick and G. B. Kistiakowsky, J. Chem. Phys. **28**, 956 (1958).
[11] Britton, Davidson, Gehman, and Schott, J. Chem. Phys. **25**, 804 (1956).
[12] Doyle Britton and Norman Davidson, J. Chem. Phys. **25**, 810 (1956).
[13] H. B. Palmer and D. F. Hornig, J. Chem. Phys. **26**, 98 (1957).

[14] R. A. Alpher and D. R. White, Phys. Fluids 2, 153 (1959), this issue.

collision theory, providing that a parameter of the theory, the "collision efficiency," is adjusted for the best fit to the data. The theory then gives a numerical value for the dissociation rate constant.

III. THEORY

We shall confine ourselves here to presenting those theories which yield rate constants within an order of magnitude of the experimentally measured value for oxygen. It can be seen from this remark that the theory of reaction rates is far from being in satisfactory condition; the difficulty is lack of understanding of what occurs in the encounters of individual particles.

The rate constants that control the dissociation and recombination of oxygen are defined by the equation

$$d[O_2]/dt = -k_{D1}[O_2]^2 - k_{D2}[O][O_2] \\ + k_{R1}[O]^2[O_2] + k_{R2}[O]^3, \quad (1)$$

where the bracketed quantities are the concentrations in moles/cc of the various species. The four different rate constants apply to the four kinds of collision processes assumed to cause reaction, which are, respectively, dissociation of one molecule in molecule-molecule and molecule-atom collisions, and recombination of two atoms in three-body collisions with a molecule and with an atom as the third body. As is well known, the rate constants are related through

$$K = k_{D1}/k_{R1} = k_{D2}/k_{R2}, \quad (2)$$

where K is the equilibrium constant.

The classical collision theory of the dissociation rate is derived in the books of Fowler[15] and Fowler and Guggenheim.[16] This theory calculates how many of the collisions between a molecule and another particle are sufficiently energetic to cause dissociation of the molecule. The result, the number Z_D of dissociations per cc per sec, is

$$Z_D = PZ(D/RT)^{\frac{1}{2}s+1}e^{-D/RT}/\Gamma(\tfrac{1}{2}s + 2). \quad (3)$$

Here T is the Kelvin temperature, R is the universal gas constant per mole divided by the molecular weight (32 for oxygen), and D is the dissociation energy (117.96 kcal/mole for oxygen, or 5.11 ev). The gamma function is a numerical factor arising in the derivation. The term $(D/RT)^{\frac{1}{2}s+1}$ is obtained
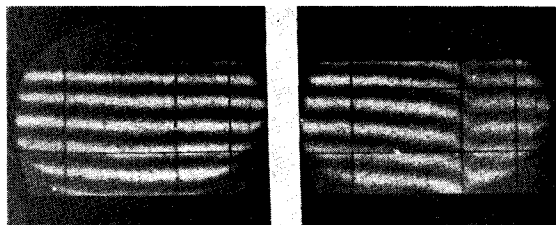

FIG. 1. Typical interferogram of shock (right) and no-flow interferogram (left). Shock is moving to right. Upward displacement of fringes indicates density increase. Discontinuous upward shift of 3 fringes occurs at shock front.

by assuming that the energy in all three translational degrees of freedom of the colliding system relative to its center of mass is available for dissociation, plus a total from both colliding particles of s square terms* in internal energy. Each rotational degree of freedom contributes one to s and each vibrational degree two. Z is the number of collisions per cc per sec computed from kinetic theory, using the molecular collision diameter of 3.6×10^{-8} cm for oxygen obtained, e.g., from viscosity measurements. Of course, $Z \propto T^{\frac{1}{2}}$. Equation (3) is the first term in the exact expression [cf. Eq. (9), page 498, reference 16]. The remaining terms are negligible if $D \gg (\tfrac{1}{2}s + 1)RT$, which is not quite true in the present case; however, it is customary to make the approximation and neglect the error. The quantity P can be called the "collision efficiency" and is the probability that a collision with sufficient energy will actually lead to dissociation. Its value has to be determined by fitting Eq. (3) to the experimental data. If the exact equation were used instead of the approximate Eq. (3), the value of P obtained would be about 10% lower, hardly a significant amount. The collision diameter and P are both assumed to be independent of temperature; their actual temperature dependence will be taken up in the value adopted for s.

The value of s is estimated by considering how much energy is available from vibration and rotation of the colliding particles. It seems extremely unlikely, considering the results of reference 5, that a large change in vibrational quantum number will occur during a single collision, even if that collision is energetic enough to cause dissociation. Therefore one might expect that all the vibrational energy of the dissociating molecule, and no more, will go into dissociation, contributing 2 to s. Since angular momentum must be conserved, at most two of the

[15] R. H. Fowler, *Statistical Mechanics* (The Macmillan Company, New York, 1936), second edition, Chap. 18.
[16] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1939), Chap. 12.

* Expressions for the kinetic and potential energy of translation, rotation, and vibration are quadratic in the position or momentum coordinates, hence this name. The s used here is twice the s of reference 15, p. 708.

four rotational square terms in two colliding molecules should be available, and when a molecule and an atom collide, no energy should be available from rotation. Thus the exponent $\frac{1}{2}s + 1$ should be about 2 to 3 in molecule-molecule collisions and about 2 in molecule-atom collisions. There is another uncertainty, however, in that only the translational energy corresponding to relative motion along the line of centers of the colliding particles may really be available. If this is so, the exponent is $\frac{1}{2}s$ only.

Theoretically, we can thus place an upper limit on s, but the lower limit is less reliable. The experimental determination of s is also unreliable because of the dominance of the Boltzmann factor in Eq. (3). However, the value of s must be chosen so that P is not $\ll 0.01$ or $\gg 1$; otherwise, the idea of "sufficiently energetic collisions" loses its meaning. The limits so placed on s by these experiments will be discussed in Sec. VII.

It will be seen that this theory is semiempirical at best. In order to improve it, one would have to consider such factors as the ground-state degeneracy of the oxygen molecule, the closer spacing of vibrational levels near the dissociation limit, and the vibrational state of the energetic colliding particles as compared with that corresponding to T. The constants s and P thus do not have an accurately defined physical meaning.

Wigner[17] has made a calculation of the recombination rate of two identical atoms in the presence of a third inert atom. This calculation is intended to give very nearly an upper bound to the recombination rate. It does not contain any adjustable parameters. It has shown rather good agreement with experimental data at temperatures $< 1000°K$. The author has computed k_R for oxygen in this way, obtaining[18]

$$k_R = 18.5 \times 10^{16} T^{-\frac{1}{2}} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}. \quad (4)$$

Keck[19] has developed a new statistical theory of reaction rates, using scattering theory in the strong coupling approximation as originally developed in nuclear physics. It covers a very wide temperature range and the various older theories form a sort of envelope of upper bounds to it. The Wigner theory forms a good upper bound at intermediate temperatures, and collision theory at higher temperatures.

Keck's paper does not present the theory in a form which can be compared with experimental results.

It is interesting that the rate of dissociation of oxygen has been successfully estimated[20] by assuming that its recombination rate is about the same as those of iodine and bromine. For this reason, the new theory of Bunker and Davidson[21] of the rate of recombination of halogen atoms may, if it is correct, be equally applicable to oxygen. The theory, like that of Wigner, involves an inert third body, but it supposes the reaction to occur in two stages. In the first stage, one of the atoms forms a Van der Waals complex with the third body; recombination occurs in the second stage, which is a collision between this complex and the other atom. There are difficulties with the theory, but it yields a result of the right order of magnitude.

Jarre[22] has calculated a dissociation rate for oxygen. The length of the reaction zone which he calculates from this rate is several thousand times less than that observed experimentally. Jarre does not explain in this paper the derivation of his rate constant.

We shall now convert Eq. (1) into a form suitable for actual comparison with measurement. If there are n atoms and N molecules, the degree of dissociation α is defined as $\frac{1}{2}n/(N + \frac{1}{2}n)$, i.e., the fraction of molecules dissociated. Then $[O_2] = (1 - \alpha)\rho/M$ and $[O] = 2\alpha\rho/M$, where ρ is the total density and M is the molecular weight of O_2. Then the equilibrium constant in terms of concentrations, $K = [O]^2/[O_2]$, becomes

$$K = \frac{4\alpha_2{}^2}{1 - \alpha_2} \frac{\rho_2}{M}, \quad (5)$$

where the subscript 2 indicates equilibrium values. Keeping in mind that the derivative in Eq. (1) is the rate due to chemical change at constant density, and changing the variable from t to x, the distance behind the shock, one obtains, writing v_1 as the velocity of the shock,

$$\frac{d\alpha}{dx} = \frac{\rho^2}{Mv_1\rho_1} \{(1 - \alpha)^2 k_{D1} + 2\alpha(1 - \alpha)k_{D2}\}$$
$$\cdot \left\{ 1 - \frac{4\alpha^2}{(1 - \alpha)KM} \right\}. \quad (6)$$

According to Eq. (5), the second quantity in braces

[17] Eugene P. Wigner, J. Chem. Phys. **5**, 720 (1937); **7**, 646 (1939).

[18] Steve P. Heims (private communication) has obtained the same result using this method. The higher value given in his report N.A.C.A. T.N. 4144 (1958) was caused by a computational error.

[19] James C. Keck, J. Chem. Phys. **29**, 410 (1958).

[20] S. W. Benson and A. E. Axworthy, Jr., J. Chem. Phys. **26**, 1718 (1957).

[21] Don L. Bunker and Norman Davidson, Tech. Rept. II-2, Department of Chemistry, California Institute of Technology, Pasadena, 1958.

[22] Gianni Jarre, Z. angew. Math. Phys. 9b, 389 (1958).

vanishes at equilibrium. The equation places no restrictions on the form of the k_D's. The k_D's actually used were Eq. (3) divided, e.g., by $[O_2]^2$ for k_{D1}, in conformity with Eq. (1).

In order to calculate a curve, $\rho = f(x)$, from this equation, we must know α as a function of ρ. This can be done, once the velocity of the shock wave and the state of the unshocked gas have been determined, by solving the equations of conservation of mass, momentum, and energy across the shock. This has been conveniently carried out by Evans[23] who actually tabulates simple functions of ρ, T, α, and the pressure p for any diatomic gas, with the shock Mach number and the enthalpy as arguments. The enthalpy of oxygen was obtained from the tabulation by the National Bureau of Standards.[24] It should be emphasized that no approximations have been made in these calculations. For example, all the modes of excitation of the particles are taken into account in the NBS tables. Again, the reaction zone is not even roughly isothermal, and the theory fully takes the temperature change into account.

The equilibrium density can be calculated from Eq. (5) for any given shock, without assumptions about the mechanism or rate of reaction. This calculated value can be compared with the measured value to provide a valuable test of the experimental accuracy.

Extensive calculations of shock profiles (extensive as distinct from those just described, which were done only for certain particular Mach numbers and states of the unshocked gas) have been carried out by Jarre,[22] Freeman,[25] and Duff.[26] The reader who wishes to visualize how the shape of the reaction zone is affected by the Mach number of the shock, the pressure, and the form of the rate constant should consult these references.

We now answer certain possible objections to this theoretical approach. Duff[26] has shown that the chain reaction mechanism involving ozone proposed by Benson and Axworthy[20] cannot contribute as much as 0.5% to the reaction rate in shock waves. As for the effect of impurities, it has been verified experimentally[7,8,11] that atoms and molecules of the dissociating gas are generally the most efficient collision partners; thus, e.g., 1% of impurity can at worst reduce the reaction rate by 1%. This contrasts with the situation in vibrational relaxation, where impurity molecules such as H_2O may be thousands of times more effective in producing relaxation than molecules of the relaxing gas, so that a small impurity may increase the relaxation rate many times.

Extrapolation of Blackman's[5] data on the rate of vibrational relaxation, following Widom's[27] suggestion that the rate increases as exp (const T), shows that it is from 30 times (at 5000°) to well over 100 times (at 3000°) faster than the measured rate of dissociation. On our photograph at the lowest Mach number, a region, less than 1 mm long as compared with a chemical reaction zone several cm in length, can be seen, which is identifiable with vibrational relaxation. Vibration is thus practically in equilibrium everywhere in the reaction zone, a statement which applies still more strongly to rotation and translation. The temperature is thus well defined at all points. Furthermore, energy lost by radiation during the reaction is negligible compared with that absorbed in the process of dissociation.

IV. TECHNIQUE

We shall confine this section to describing those features of the apparatus which are important to understanding the results. A more detailed description may be found in the author's thesis,[28] of which this paper is a somewhat abridged version.

The shock waves were produced using hydrogen or helium as the driver gas and strengthened by means of convergence in the test section as first used by Blackman.[5] The driver section was 4.5 ft long and circular in cross section, having an inside diameter of 3.2 in. There was no change in shape or size at the diaphragm. The first part of the low-pressure section was 11 ft long and was followed by convergence to 2 ft of rectangular test section, $\frac{3}{4}$ in. high and $1\frac{3}{8}$ in. wide, inside. The windows were effectively $1\frac{5}{8}$ in. long $\times$ $\frac{3}{4}$ in. high.

The oxygen used was an ordinary commercial grade containing about 0.5% impurity. Further impurity not exceeding 0.6% was caused by air leaking into the shock tube between the times of admitting the test gas and firing the shock. The pressure before firing, from 10 to 20 mm, was measured to 1%, and the temperature to 0.3°C.

Thin-film resistance thermometers, identical in principle with those developed by Chabai and Emrich[29] and by Blackman,[5] were used to detect the passage of the shock. Pulses from these detectors

[23] John S. Evans, Tech. N.A.C.A. T.N. 3860 (1956).
[24] Hilsenrath, Beckett, Benedict, Fano, Hoge, Masi, Nuttall, Touloukian, and Woolley, Circular 564, National Bureau of Standards, Washington, D. C., 1955.
[25] N. C. Freeman, J. Fluid Mech. 4, 407 (1958).
[26] Russell E. Duff, Phys. Fluids 1, 242 (1958).

[27] B. Widom, J. Chem. Phys. 27, 940 (1957).
[28] D. L. Matthews, Ph.D. thesis, Princeton University, Princeton, New Jersey, 1958.
[29] A. J. Chabai and R. J. Emrich, J. Appl. Phys. 26, 779 (1955).

were displayed on a trace together with crystal-controlled 5-μsec markers, and the result photographed. The detectors were 35 cm apart so that the detector pulses were separated by $\sim$ 100 μsec. Additional detectors within those outside ones gave information about the constancy of the shock velocity. Slight lack of this constancy was the main cause of an estimated error of 1% in the measured velocity and therefore in the Mach number.

Under the conditions of these experiments, these detectors reach the limit of their usefulness near a shock Mach number of $M_1 = 10.5$, when spurious extra pulses appear, probably caused by ionization. These extra pulses appeared on some of our timing traces, but as they were separated from the real pulses by several microseconds, ambiguities could be resolved by comparing the equilibrium density observed in the interferometer with those calculated from the two possible shock velocities. One and only one of the possibilities always gave about 1% agreement, the same agreement which was observed when spurious pulses were absent.

The pulse from the first detector was used to trigger a time-delay generator, set to have its delayed output fire the spark light source when the shock was in the window. This spark light source had an effective duration, as estimated from the observed thickness of the shock, of 0.1–0.2 μsec.

A Mach-Zehnder interferometer having a field flat to better than one fringe was used to observe the density in the region of the shock. A band of wavelengths around 3700 A was selected by a Wratten filter. Only about 12 good fringes are produced by such a filter, but the total fringe shift did not exceed six in any experiment. This fact makes it possible to dispense with white-light fringes, the experimental accuracy being such that no ambiguity is possible about the integral fringe shift across the shock.

A static calibration of the interferometer was made to obtain the (linear) relationship between fringe shift and density, the position of the fringes being photographed with oxygen in the tube at different measured pressures. This calibration was considered accurate to $\pm 1\frac{1}{2}\%$.

The work of Alpher and White[14] has shown that in oxygen no correction needs to be applied to such a calibration when the oxygen is dissociated, within a few percent for full dissociation, or within less than 1% in our experiments.‡

At this stage we make a brief comparison with the

‡ One must expect in general to apply a correction and in nitrogen, for example, it is quite large.

method of Byron,[7] who was the only other experimenter to use an interferometer to measure the dissociation rate of oxygen. His results will be discussed in Sec. VI. The following differences in method were significant: (a) Byron used a spark of long duration and projected the fringes onto the slit of a rotating drum camera, so that fringe displacement was measured as a function of time instead of distance. The resolving time obtained was not much less than 1 μsec, i.e., it was about 4 times longer than ours. Otherwise, the two methods are the same in principle, since the shape of the reaction zone does not change with time. (b) The interferometer was placed horizontally rather than vertically and both beams were allowed to pass through the shock tube. When the shock passes the second window, the fringes, which were suddenly displaced when it passed the first window, revert suddenly to their original position. The shock velocity is determined from the camera speed and the separation of the two discontinuities on the film. (c) In addition to pure oxygen, Byron used oxygen greatly diluted with argon, a device which enabled him to get rate constants with the argon or the oxygen atom as the agent causing dissociation.

V. INTERPRETATION OF DATA

The data are in the form of interferograms like Fig. 1, together with timing traces and the pressure and temperature of the unshocked gas. It only remains to describe the method of obtaining the gas densities from the interferograms. The density ratio across the shock front at vibrational equilibrium and no dissociation—that part of the density change which is seen as a discontinuous jump—was about seven, corresponding to a jump of about one to three fringes, depending on the initial density. The equilibrium density ratio was, by coincidence, very nearly equal to the Mach number of the shock, so that the fringe shift in the reaction zone was 0.5 to 1.3 fringes. In the reading of the interferograms, the fringe position at a number of distances from the shock front was carefully compared with the fringe position at the corresponding place on the "blank" interferogram (also shown in Fig. 1) which was taken about a minute before firing the shock. In this way errors arising from lack of straightness of the fringes were practically eliminated. The blank was also checked against the section in the flow picture not yet reached by the shock, and any difference taken into account. Such differences, which are usually less than 0.1 fringe and uniform over the field, are thought to be caused by waves
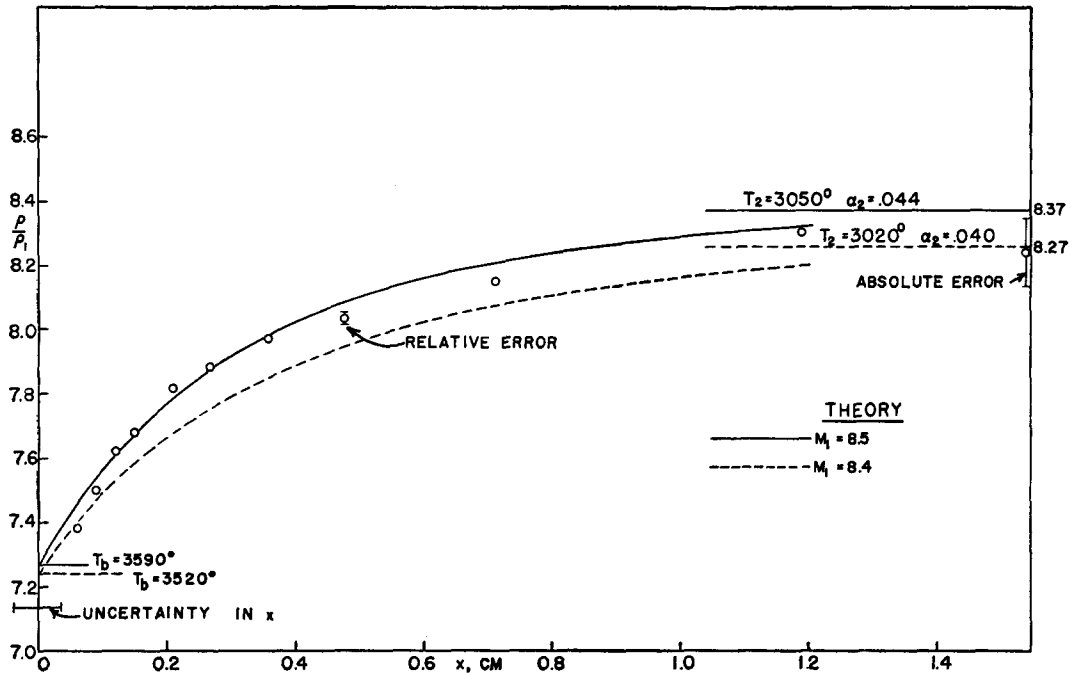
FIG. 2. Theoretical and experimental density ratios for $M_1 = 8.5$, $p_1 = 19.6$ mm. Theoretical curve for $M_1 = 8.4$ also shown. T_1 was room temperature, $\sim 22°C$, in all experiments.

propagated along the solid structure of the shock tube and arriving ahead of the shock itself.

The measured fringe shift was considered accurate to $\pm$ 0.03 fringe and sensitive, in more or less adjacent regions, to changes of less than 0.02 fringe.

Figures 2 and 3 show the density ratio across the shock, ρ/ρ_1, computed from the measured fringe shifts at shock Mach numbers M_1 of 8.5 and 10.2. It should be noted that the range of density ratios from 0 to 7 is suppressed so that only the zone of chemical reaction is displayed. The observed uncertainty in position of the shock, i.e., in the zero of x, is shown at the left of each figure. This uncertainty arises mainly from the finite duration of the spark. One of the two vertical error flags indicates the accuracy of the points relative to one another, as determined by the accuracy of measuring the interference fringes, while the other larger flag shows the estimated over-all reliability of the measurement of ρ/ρ_1 near equilibrium. The relative scales are not the same in the two figures. These figures also show theoretical curves, calculated by collision theory and Eq. (6), using the experimentally determined Mach number of the shock and state of the unshocked gas. The subscript b indicates vibrational equilibrium but no dissociation, while 2 indicates full equilibrium. The room temperature T_1 was measured each time and was usually about 295°K. The calculated pressure increases only about
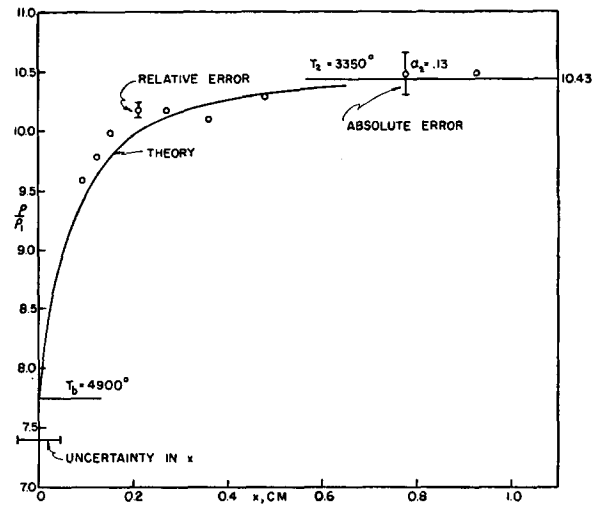

FIG. 3. Theoretical and experimental density ratios for $M_1 = 10.2$, $p_1 = 10.0$ mm.

5% from zero to equilibrium dissociation, so that the ordinate is nearly proportional to $1/T$.

No relaxation times are presented here. They are hard to define in shock-induced dissociation, because it is far from being an exponential process and because the degree of dissociation at equilibrium depends upon the pressure p_1 ahead of the shock. An expression for the relaxation time has, however, been defined by Duff,[26] who discusses the above difficulties.

In calculating the rate constants from Eq. (3), we have taken the power of D/RT as $\frac{1}{2}s + 1 = 3$ for molecule-molecule collisions and 2 for molecule-atom collisions. There were few $O_2 - O$ collisions compared with $O_2 - O_2$, so that the efficiency P_{at} for $O_2 - O$ collisions could not be experimentally determined. In making the calculations, the ratio P_{at}/P_{mol}, where P_{mol} is the efficiency for $O_2 - O_2$ collisions, was determined from the constants used by Byron[7] to fit his data. Byron was able to separate out the effect of $O_2 - O$ collisions by using oxygen-argon mixtures, in which a much higher degree of dissociation is obtainable than in pure oxygen with a shock of given Mach number. If Byron's value for P_{at}/P_{mol} is correct, the maximum contribution to the reaction rate in our experiments from $O_2 - O$ collisions is about one-quarter of the total rate. When P is mentioned from here on, P_{mol} is what is meant.

Inspection of Eq. (6) shows that after it has been integrated (this was done numerically) x is inversely proportional to P, since the k_D's are proportional to P. The value of P was chosen to give the best average fit of the curves to the experimental points, and was based on a total of eight experiments, including those of Figs. 2 and 3. The same value of P was used for all the pictures, and it was the only parameter whose value was adjusted to fit the data. The theoretical curves in Figs. 2 and 3 were calculated using this value of P.

In comparing the theoretical curves with the experimental points, one should note that an increase in M_1 of 0.1 (about 1%) will increase the slope of the theoretical curve by about 30%. Since the probable error in M_1, excluding possible systematic error, is of this order, the results show satisfactory consistency. The figure of 30% can be arrived at by considering the initial rate (for $\alpha = 0$). At $T_b = 4000°$, say, an increase in M_1 of 0.1 raises the initial temperature T_b by about 75°. The rate of increase of density is nearly proportional to $\exp(-59\,380/T)$. In Fig. 2, theoretical curves for $M_1 = 8.5$ (the measured value) and 8.4 display this effect, including the effect on the calculated equilibrium density. The magnitude of the effect is about the same throughout the experimental range.

It can be seen from the scatter of the experimental points that there are small nonuniformities in the flow. Their random effect is evidently small compared to that of dissociation. Any possible systematic effect has been neglected on the grounds that (a) constant density, within the scatter, is observed in the whole observable equilibrium zone, which at the

higher Mach numbers is several times longer than the reaction zone, and (b) an experiment in argon at $M_1 = 7$, where the ionization is vanishingly small, showed similarly constant density beginning at the shock itself.

Inspection of the graphs shows that the uncertainty in the rate due to random errors is about 20%. As for possible systematic errors, we can see that, as remarked earlier, there is good agreement, to about 1%, between interferometrically observed equilibrium density and that calculated from the observed Mach number. This 1% in density ratio corresponds to 1% in M_1, or about 30% in the rate. Taking into account random and possible systematic errors, we shall assign limits of estimated error to P one of which is twice the other, with the value of P obtained from the experiments as their geometric mean.

VI. RESULTS

The rate constant for dissociation which we conclude fits the data is

$$k_{D1} = 7.43 \times 10^{11}\, PT^{\frac{1}{2}}(59\,380/T)^3$$
$$\cdot \exp(-59\,380/T)\ \text{cc mole}^{-1}\,\text{sec}^{-1}, \quad (7)$$

in which $P = 0.073$, or within estimated limits of error, $0.05 < P < 0.1$. If the power of D/RT is assumed to be 2 instead of 3, $P = 0.35$.

Values of the rate constant in oxygen are presented in Figs. 4 and 5. Those investigations (including this one) whose results have been presented as dissociation rates are shown in Fig. 4. The curves are a result of the authors having fitted collision theory, with 2 or 3 as the exponent of D/RT, to experimental data. The two experimental points obtained by Chesick and Kistiakowsky[10] are also shown on this graph. These workers used a mixture of 25% Xe and 75% O_2 in a shock tube. They consider that only the average of the two measurements is significant.

In Fig. 5, all the known results except those of Glick and Wurster are presented as recombination rate constants. Glick and Wurster intended only to obtain the rate within an order of magnitude, which they were successful in doing. They were the first to measure the rate. The experimental accuracy of all the other experimental investigations, although not usually stated explicitly by the authors, is thought to be about the same: that is, within a factor of 2. Note that this is also the order of agreement among the different experimental investigations.
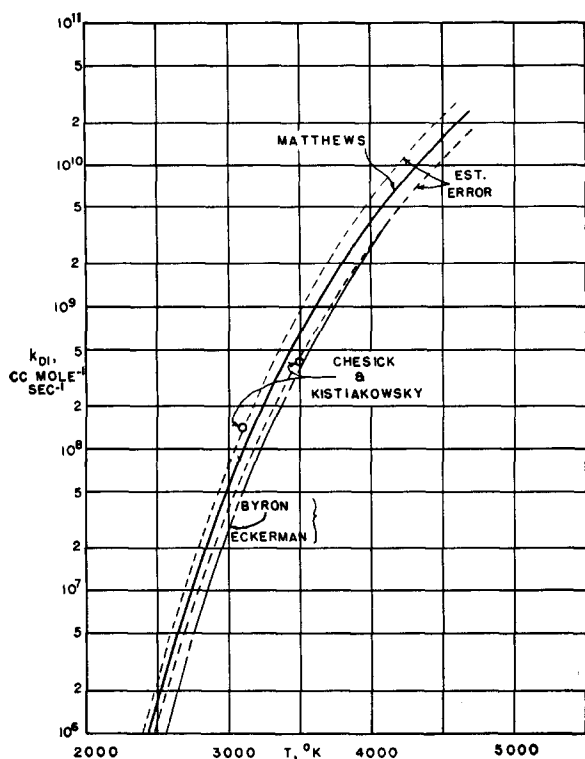
Figure 5 also shows the author's calculation using

FIG. 4. Dissociation rate constant of O_2, experimental. Curves result from fitting classical collision theory to experimental data.

FIG. 5. Recombination rate constant O_2, experimental and theoretical. All are experimental except those marked. Evans, Logan, and Camac stated constant values because of the uncertainty of the temperature dependence.

Wigner's method. It should be remarked that Wigner assumed the third body to be a hard sphere, which is a better approximation to, e.g., an argon atom than to an oxygen molecule or atom. The rate constants obtained experimentally by Byron[7] and by Camac et al.,[8] using oxygen greatly diluted with argon, were several times lower than those in pure oxygen.

Theoretical calculations by Evans[23] and by Logan[30] yielded practically the same result, which is shown in Fig. 5.

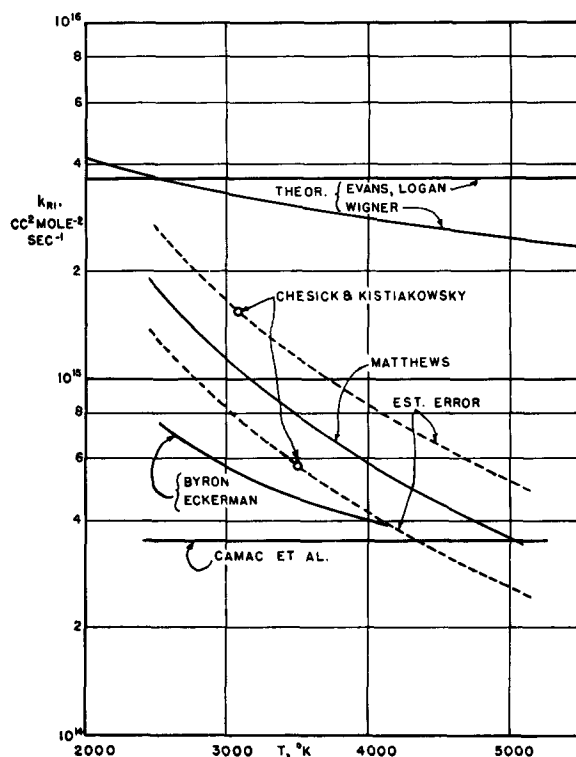Extrapolation of these recombination rates to lower temperatures is of course risky, since the temperature dependence is uncertain and may be different near room temperature from its value at high temperatures. Table I is a partial list of recombination rates in some pure gases as measured by different methods, compared with the extrapolated shock-tube results for oxygen. The extrapolation in each case was carried out with the same temperature dependence as used in the experimental region. Evidently, the shock-tube experiments give little information about the rate of recombination of oxygen at room temperature. Table I says nothing about temperature dependences or the effect of

TABLE I. Recombination rates of some pure gases.

Gas	Method	300°	k_R, cc^2 mole^{-2} sec^{-1} 1400°	3500°	Reference
O_2	Shock tube	150×10^{15} (extrapolated)	5×10^{15} (extrapolated)	0.8×10^{15}	This paper
O_2	Shock tube	6×10^{15} (extrapolated)	1.3×10^{15} (extrapolated)	0.5×10^{15}	7
Br_2	Shock tube	...	1×10^{15}	...	13
I_2	Shock tube	...	$< 13 \times 10^{15}$	...	11
I_2	Flash photolysis	1900×10^{15}	...	...	21
N_2	Afterglow	6.3×10^{15}	...	...	31

[30] J. G. Logan, Preprint 728, Institute of the Aeronautical Sciences, New York, 1957.

different third bodies in the recombination process; these topics are discussed in the references. It is noteworthy that the experiments on the recombination of N_2[31] at room temperature showed no difference in the effectiveness of N_2 and A as third bodies. In iodine, on the other hand, it appears that at room temperature I_2 is about 600 times as effective as A as a third body in producing recombination.

VII. CONCLUSIONS

The measured rate of dissociation of essentially pure oxygen is adequately fitted by classical collision theory (see Sec. III) within each shock reaction zone and also over the whole experimental range. This result leads us to conclude that the reaction $O_2 + O_2 \rightleftarrows 2O + O_2$, which is dominant in the theory, is the chief one in the dissociation process.

As has been said, the value of s, which is a measure of how much internal energy is available for dissociation, is ill defined. However, if s is taken to be zero (that is, the exponent of D/RT to be unity),

and a value of P is chosen to fit the data at $M_1 = 8$, then at $M_1 = 10$ the theoretical curve definitely reaches equilibrium in a shorter distance than do the experimental points. Furthermore, when $s = 0$, the value of P at $M_1 = 9$ is about 2, which seems rather large. The experiments thus indicate quite strongly that $s > 0$, and therefore that at least some fraction of the internal energy of the colliding molecules is available to cause dissociation. This conclusion assumes that the kinetic energy in all three translational degrees of freedom is available. If it is not all available, the energy must come from internal modes instead, and the conclusion is strengthened.

[31] Harteck, Reeves, and Mannella, J. Chem. Phys. **29**, 608 (1958).