KINETICS OF O₂ DISSOCIATION AND RECOMBINATION*

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Shock tube investigations of relaxation processes in O_2 and O_2–Ar mixtures have been carried out for several years at our laboratory. Here we briefly review the techniques utilized, the results obtained, and give more detailed comparisons with other work. Three experimental programs have been carried out employing the uv absorption technique to measure the O_2 concentration.

The first experiment dealt with the dissociation rate of O_2 by Ar catalysts from 5000 to 18,000°K. It was found that there exists an incubation time (of the order of a vibrational relaxation time) before the O_2 dissociates. When this data is used in conjunction with the subsequently obtained recombination data, a $T^{-\frac{1}{2}}$ pre-exponential factor was clearly indicated for the rate constant expression which is

$$k_d = 4.2(\pm 14\%) \times 10^{-8} T^{-\frac{1}{2}} \exp(-D/RT) \text{ cm}^6/\text{particle}^2 \cdot \text{sec}.$$

The second experiment measured the recombination rate of O atoms by Ar catalysts between 1500 and 3000°K. The excess O atoms were produced by shocking dilute O_3–Ar mixtures. At 2000°K the measured recombination coefficient k_r is about 0.7×10^{-34} cm⁶/particle²·sec. This study, with the previously mentioned dissociation work, showed that $K_{eq} = k_d/k_r$.

The third investigation involved the details of the shock front structure in O_2 from Mach 4–21. Between Mach 4 and 10 translational and rotational processes occurred simultaneously within the shock front. Between Mach 10 and 14 vibrational relaxation moved up to and finally was swallowed by the "shock front." Around Mach 16 the dissociation process started within the "shock front."

The shock tube k_d results for Ar catalyst, when extrapolated to 300°K, compare well with recombination studies. But the high catalytic efficiencies for O and O_2 found around 5000°K (Ar:O_2:O $\approx 1:18:50$) are not apparent at 300°K. For O_2 the extrapolated high temperature work is about 40 times that measured at 300°K, while that for O atoms is 100–800 times that reputed to be measured at 300°K, depending on how the extrapolation is made. Although there is some doubt as to whether the catalytic efficiency of the O atom has been correctly measured at 300°K, estimates of its value by reinterpretation of other work in the literature still fails to close this gap to better than a factor of 10. It is suggested that for the chemically-active catalyst O and O_2 the temperature dependence changes markedly between 300°K and approximately 3000°K.

Introduction

The purpose of this paper is to attempt to bring together some of the recent experimental results on O_2 dissociation and recombination. The dissociation studies are carried out at high temperatures in shock tubes, some recombination work has been done in shock tubes at intermediate temperatures, and some recombination investigations have been done at room temperature. Of particular interest are the questions: (1) What is the effect of vibrational relaxation processes on the rate of dissociation? (2) Is the recombination rate properly given by the ratio of the dissociation rate to the equilibrium constant? (3) For strong shock waves, do the vibrational and dissociative processes await translational and rotational equilibrium? (4) What are the relative catalytic efficiencies of various collision partners?—and finally—(5) How do the high temperature experiments, extrapolated to room temperature, compare with the low temperature recombination measurements?

Shock tube investigations concerning these questions have been carried out for several years

at this laboratory.[1,2,3] In this paper we will briefly review the techniques utilized, the results obtained, and give more detailed comparisons with other people's work. We consider here only the catalysts Ar, O_2, and O.

In particular, three specific experimental programs have been carried out utilizing shock tubes and employing the uv absorption technique to measure the O_2 concentration. This technique involves the measurement of I/I_0, the fraction of light transmitted through the gas sample, which is related to the concentration of the absorbing species by the Beer–Lambert law:

$$I/I_0 = \exp\{-k(T_v)l(P_1/P_0)(T_0/T_1)(\rho/\rho_1)[O_2]\}.$$

$$(1)$$

Here $k(T_v)$ is the absorption coefficient of the absorbing species per cm of path length at a density corresponding to 1 atm and 300°K; l is the optical path length; P_1, T_1, and ρ_1 are the pressure, temperature, and density in the unshocked gas, $P_0 = 1$ atm and $T_0 = 300°$K and $[O_2]$ is the dimensionless concentration of O_2, expressed in moles per original mole.

The first experiment dealt with the dissociation rate of O_2 by Ar catalysts from 5000 to 18,000°K.[1] This work was specifically carried out to investigate the coupling of the vibrational and dissociation processes. It was found that there exists an incubation time before the O_2 dissociates at its ultimate rate, this incubation time being of the order of a vibrational relaxation time. The second experiment measured the recombination rate of O atoms by Ar catalysts between 1500 and 3000°K.[2] This study, with the previously mentioned dissociation work, showed the dissociation and recombination rate constants to be related through the equilibrium constant. The third investigation involved the details of the shock front structure in pure O_2.[3] Here it was shown that between Mach 4 and Mach 10 translational and rotational processes occurred simultaneously within the shock front. Between Mach 10 and 14 vibrational relaxation was seen to move up to the shock front and at higher Mach numbers the vibrational process occurs completely within the "shock front." Around Mach 16 the dissociative process is observed to start within the "shock front."

In this paper we shall frequently make use of the equilibrium constant to compare dissociation and recombination rate constants. Given below are two analytic expressions, with their temperature range of validity, which were obtained by fitting the equilibrium constants computed from the partition functions. For the range[2]

$$300°K < T < 3500°K$$

$$K_{eq} = 10^{22}T\{1.78 - 0.80(T/1000)$$
$$+ 0.111(T/1000)^2\}\exp(-D/RT), \quad (2)$$

and for the range[4] $3000°K < T < 8000°K$

$$K_{eq} = 7.2 \times 10^{26}T^{-\frac{1}{2}}\exp(-D/RT) \text{ particles/cm}^3.$$
$$(3)$$

Here, as in all the rate expressions given in this paper, $D = 118,000$ cal/mole and $R = 1.987$ cal/mole °K. Rate constants are given in units of cm³/particle·sec and cm⁶/particle²·sec for dissociation and recombination, respectively.

Experimental Techniques

The coupling and shock front experiments were carried out in the 24-in.-diam stainless-steel shock tube available at this laboratory.[5] This facility can operate at initial pressures as low as 10 μ of Hg. The experiments carried out in the 24-in. tube involved binary processes at high temperatures which required low initial pressures in order to obtain the necessary resolution.

At such low densities the shock front curvature thickness δ_0 is appreciable. Lin and Fyfe[5] have studied this phenomenon and give results which yield[1]

$$\delta_0(\text{mm}) = 1.75P_1^{-\frac{1}{2}}(\text{mm of Hg}). \quad (4)$$

The effect of shock front curvature can be minimized by the knife-edge technique which restricts the observation to the central portion of the shock-heated gas.[1] The effective shock front curvature thickness δ is then given by

$$\delta = \delta_0(l/D)^2, \quad (5)$$

where l is the optical path length between knife-edges and D is the shock tube diameter. In general, for these absorption experiments the resolution of the detection system τ_{res} is simply the transit time of the curved shock front across the finite slit, hence

$$\tau_{res} = (S + \delta)/U_s, \quad (6)$$

where S is the slit width, and U_s is the shock velocity.

A schematic diagram of the shock tube test section is shown in Fig. 1. The light source used on the 24-in. tube was a pulsed helium discharge lamp (Lyman Lamp).[6] This light source produces an oscillating light output whose maximum intensity could be considered to be flat for about 15 μsec. The knife-edged plates (see detail, Fig. 1) were designed to minimize aerodynamic disturbances.[1] Also shown in the sche-
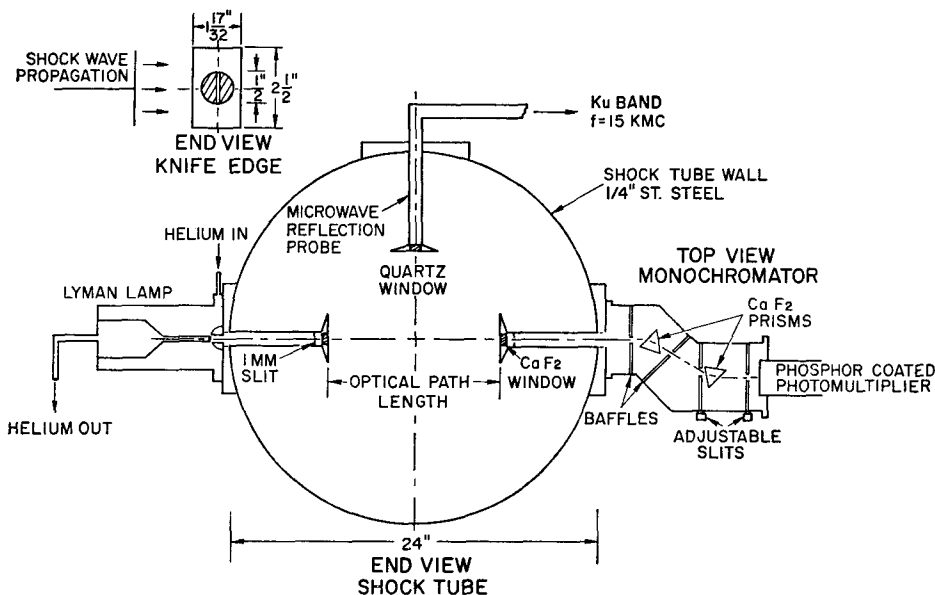
FIG. 1. Schematic diagram of the shock tube test section. Both the uv optical system and the microwave system are shown.

matic diagram is a microwave reflection probe which was used only in the coupling experiment.

The recombination experiment required high initial pressures due to the fact that the process being investigated proceeds by 3-body collisions
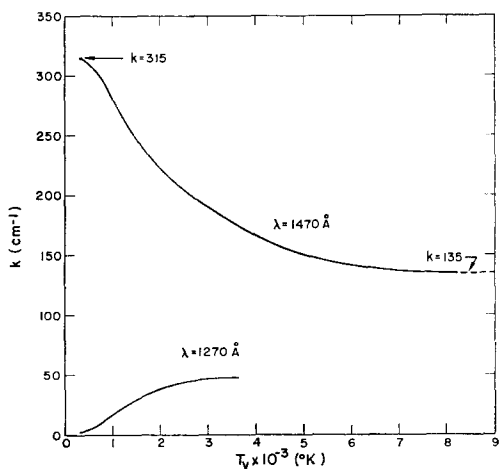

FIG. 2. The experimentally determined absorption coefficient per cm of path length at a density corresponding to 1 atm and 300°K plotted against the vibrational temperature. Curves are shown for radiation of 1470 Å and 1270 Å. Measurements at 1470 Å were made only to 8000°K; however, theoretical arguments indicate a constant value thereafter.

and hence is relatively slow. Thus, this experiment was carried out in a conventional 1½-in.-diam shock tube at initial pressures of ¼ to 1 atm. At such high pressures there was no need to employ knife edges. Even at the high pressures used here recombination times were of the order of 100 μsec and hence this work utilized a hydrogen light source[6] whose intensity rose rapidly to a maximum and then decayed monotonically to zero in several milliseconds. This experiment employed radiation at 1270 Å.

The room temperature, i.e., vibrationally unexcited, absorption coefficient of O$_2$ was obtained simply by measuring the attenuation of the uv light beam as a function of O$_2$ pressure in the shock tube. The absorption coefficient for the vibrationally excited molecule was obtained by making shock tube runs in dilute O$_2$-Ar mixtures and observing the signals subsequent to vibrational relaxation but before a finite amount of dissociation had occurred. Such a state of the gas is only obtainable at temperatures up to about 8000°K. The absorption coefficients of O$_2$ as a function of vibrational temperature determined in the above manner are plotted in Fig. 2 for 1470 Å[6] and 1270 Å[2] radiation.

The Coupling of Vibrational Relaxation and Dissociation

The O$_2$-Ar results of Camac and Vaughan[7] indicated that the ratio of the dissociation time

to the vibrational relaxation time τ_d/τ_v, at 5000°K was 60 while if one extrapolated their analytical rate expressions to 18,000°K, $\tau_d/\tau_v = 1.4$, indicating a substantial amount of dissociation prior to vibrational equilibrium. The purpose of this investigation was to see how the dissociation process was affected by this lack of vibrational equilibration. Three O_2–Ar mixtures were used, containing 4% $O_2(P_1 \sim \frac{1}{4}$ mm), 2% $O_2(P_1 \sim 1$ and $\frac{1}{2}$ mm) and 0.5% $O_2(P_1 \sim 4$ and 10 mm). The temperature range covered was 5000–18,000°K. In these experiments the slit width was 1 mm and the optical path length l was 1 ft so that $\delta/\delta_0 = \frac{1}{4}$. Resolution times cal-

culated from Eq. (6) agreed well with the experimentally determined signal rise time.

At the high temperature end of the range of these experiments, equilibrium ionization of the Ar diluent is appreciable and would represent a temperature decrease of many thousands of degrees. The pertinent question here is whether or not this ionization occurred during or subsequent to the dissociation of the oxygen. Microwave reflection measurements showed that over the entire temperature range investigated the ionization took place subsequent to the dissociation process and hence was ignored in the data reduction.
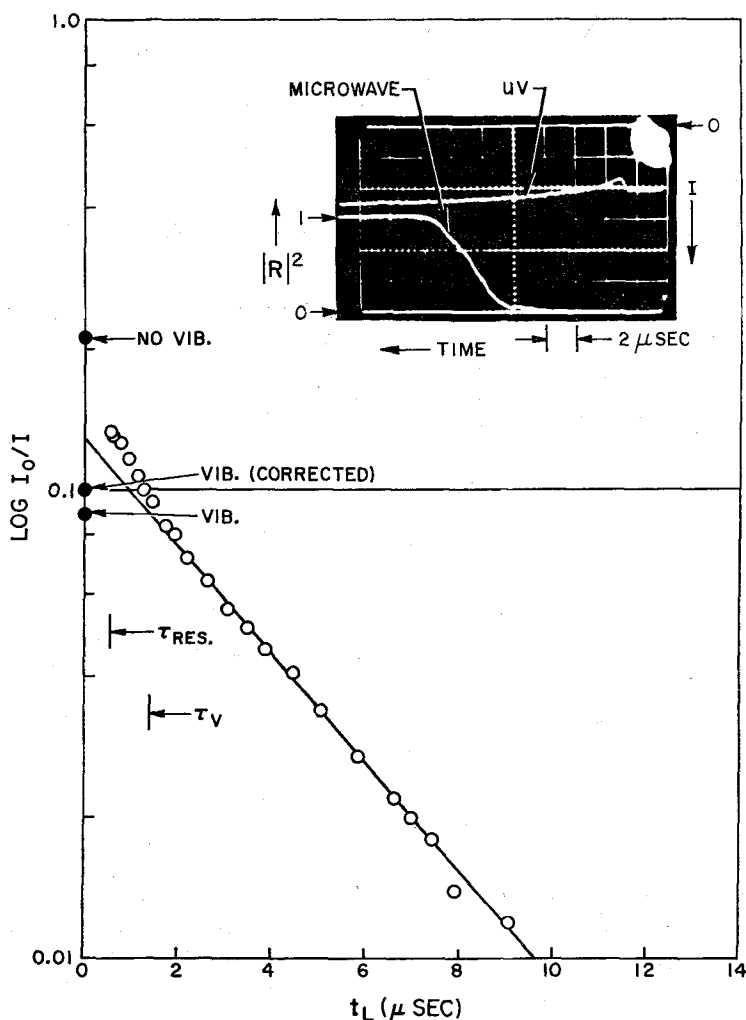

FIG. 3. LogI_0/I plotted against laboratory time for a particular shock tube run in the O_2–Ar dissociation experiment. The inset shows the oscillogram from which this plot was prepared. Indicated in this figure are the resolution τ_{res} and the vibrational relaxation time τ_v. For other notations see the text. Shock conditions: 4% O_2–96% Ar, $P_1 = 0.236$ mm, $U_s = 3.53$ mm/μsec, $T = 10,545$°K.

For mixtures studied in this experiment the density and temperature behind the shock front are essentially constant, and consequently the absorption coefficient also becomes constant once vibrational equilibrium is obtained. Hence, as dissociation proceeds, $[O_2]$ is the only variable affecting the absorption given by Eq. (1). It can be shown that under these conditions the following equation is applicable[1]

$$d \log (\log I_0/I)/dt_L = -(k_d/2.3) n_{Ar}(\rho_2/\rho_1), \quad (7)$$

where t_L is the time in the laboratory coordinate system, n_{Ar} is the number of argon atoms/cm³, and ρ_2/ρ_1 is the density ratio across the shock. This equation indicates that a semilog plot of $\log I_0/I$ vs t_L should be a straight line whose slope yields the dissociation rate constant k_d.

A typical oscillogram obtained in this work along with the data obtained from it is shown in Fig. 3. The oscillogram shows both the uv absorption record which monitors the oxygen concentration and the microwave reflection signal $|R|^2$ which monitors the electron concentration. Indicated on the figure are τ_{res}, obtained from Eq. (6) and the vibrational relaxation time τ_v,
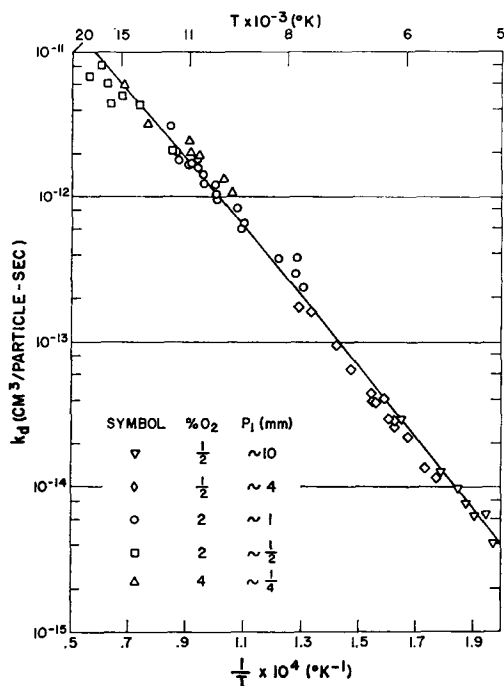

FIG. 4. The rate constant for the dissociation of O₂ by Ar plotted against reciprocal temperature. The least-squares fit to the data shown by the solid line yields $k_d = 4.2 \pm (14\%) \times 10^{-8}T^{-\frac{1}{2}}$ exp $(-D/RT)$.

extrapolated from the work of Camac.[6] In all cases the data led to straight lines when plotted in the manner indicated, except for $t < \tau_v$ for runs where $\tau_v > \tau_{res}$, as it is for the case illustrated in Fig. 3. This deviation from the straight line behavior is due to the fact that for $t < \tau_v$ the absorption coefficient k is not a constant and Eq. (7) is not applicable. The point labeled "no vib" on the time equal zero axis is computed from Eq. (1) setting $k(T_v) = 315$ and would be where the real data would have to extrapolate back to zero time. The point labeled "vib", calculated using a $k(T_v)$ obtained from Fig. 2 $(\lambda = 1470$ Å), would be where the straight line portion of the data would have to extrapolate in order to maintain the same slope back to zero time. The point labeled "vib (corrected)" is a similarly computed point corrected for the effect of finite slit width and shock front curvature. For details of this correction, see Ref. 1. The time Δt at which the extrapolated experimental line crosses the ordinate "vib (corrected)" represents a time during which the dissociation process is inhibited.

Figure 4 is a plot of the rate constant for dissociation of O₂ by Ar catalysts plotted against reciprocal temperature. The data points shown here were all obtained from the slopes of curves such as that shown in Fig. 3. The solid line is a least squares fit to the data of the present experiment and leads to the following rate constant expression

$$k_{Ar} = 4.2(\pm 14\%)$$

$$\times 10^{-8}T^{-\frac{1}{2}} \exp (-D/RT) \text{ cm}^3/\text{particle} \cdot \text{sec.}$$

$$(8)$$

The $T^{-\frac{1}{2}}$ pre-exponential factor is not well determined here (T^{-1} fits almost as well), but is used in the light of the recombination experiment to be described later.

It should be mentioned here that the shape of the $\log I_0/I$ vs time curves at the highest temperatures of this experiment rule out the very high catalytic efficiencies for O and O₂ relative to Ar which clearly exist at temperatures around 5000°K.

The incubation times obtained from the data plots as explained above decreased by more than 2 decades between 5000 and 18,000°K. The incubation time data can be made nondimensional and density-independent by normalizing with the vibrational relaxation time. The incubation time data treated in this manner are shown in Fig. 5. Although the scatter in the data is considerable the results clearly indicate that the dissociation rate of O₂ is severely limited until some vibrational relaxation has occurred,
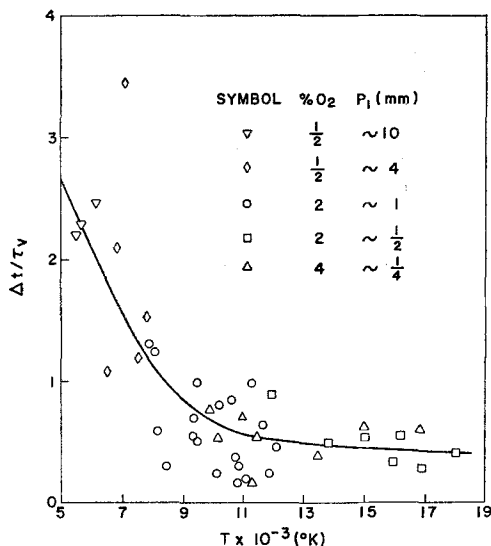
FIG. 5. The incubation time divided by the vibrational relaxation time, plotted against temperature. The solid line is a subjective fit to the data.

the amount of relaxation necessary being larger at lower translational temperatures.

Recombination of O Atoms by Ar Catalysts

In order to study recombination of atoms at high temperatures it is obviously necessary to produce an overabundance of atoms in a hot gas. This was accomplished by shock-heating dilute mixtures of O_3 in Ar. The thermal decomposition of O_3 has been studied by several investigators and the mechanism and rate constants are available in the literature.[8,9] The decomposition proceeds in the following manner:

$$O_3 + Ar \rightarrow O + O_2 + Ar, \qquad \text{(I)}$$

$$O + O_3 \rightarrow 2O_2. \qquad \text{(II)}$$
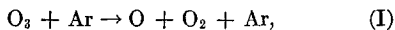
At high Ar concentrations and high temperatures Reaction (I) can be made sufficiently fast so that Reaction (II) does not play any significant role before the O_3 is completely decomposed. Under these conditions, if the temperature is not too high, the O atoms produced by Reaction (I) must recombine via the reaction

$$O + O + Ar \rightarrow O_2 + Ar. \qquad \text{(III)}$$
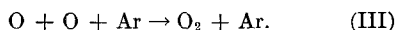
Of course, if the temperature is too high the O_2 produced in (I) will dissociate by the reverse of (III). If the temperature is too low Reaction (II) consumes the oxygen atoms produced by Reaction (I) so that Reaction (III) does not play any role whatsoever. These two conditions

limit the temperature over which the recombination rate could be measured by this technique to between 1500 and 3000°K. For the conditions of the experiment, (I) is extremely fast compared to (III), the O_3 decomposing in fractions of a microsecond. Three mixtures were studied: 0.25% O_3 ($P_1 = 80$ cm), 0.5% O_3 ($P_1 = 40$ cm) and 1% O_3 ($P_1 = 20$ cm). Again, for these mixtures conditions behind the shock front are essentially isothermal and isobaric.

Because the recombination times were long, the nonoscillating (but less intense) hydrogen lamp was used. The decreased intensity was compensated for by using 2-mm-wide slits and integrating the signals for several microseconds. Because of the high partial pressures of O_2 being monitored in this experiment, 1270 Å radiation was used because of its lower absorption coefficient (see Fig. 2).

For the three-body recombination with a constant Ar-catalyst concentration it is readily shown that[2]

$$\alpha^{-1} = 6(\rho_2/\rho_1)n_{Ar}^2 f k_r t_L + 3, \qquad (9)$$

where α is the fraction of oxygen dissociated, f the fraction of O_3 in the O_3–Ar mixture, and k_r the recombination rate constant. The constant of integration in the above equation results from the fact that Reaction (I) produces an equal molar mixture of O and O_2 at the shock front. α itself can be computed at any time from the equation[2]

$$\alpha = \tfrac{1}{3} - (2/3k_{O_2}C) \ln (I_{SF}/I_t), \qquad (10)$$

where k_{O_2} is given in Fig. 2 (1270 Å), and I_{SF}/I_t is the ratio of the transmitted light intensity at the shock front (after Reaction (I) has gone to completion) to that at time t, and

$$C = l(P_1/76)(300/T_1)(\rho_2/\rho_1)f. \qquad (11)$$

Figure 6 shows a plot of α vs t_L for a typical run obtained in this experiment. According to Eq. (9) these data should fall in a straight line whose slope will yield the recombination coefficient. In general, plots of this type were found to yield good straight lines up to times of about 60 μsec and in all cases the data points then fell below the extrapolated straight line. This deviation is caused by shock wave attenuation, disappearance of oxygen atoms (which have a higher catalytic efficiency), and the onset of the reverse of Reaction (III) as the system approaches equilibrium.

The rate constants obtained in the above manner are plotted in Fig. 7 as a function of temperature. Also plotted in Fig. 7 are the O_2–Ar dissociation data points of Fig. 4 divided by the equilibrium constant. There are four
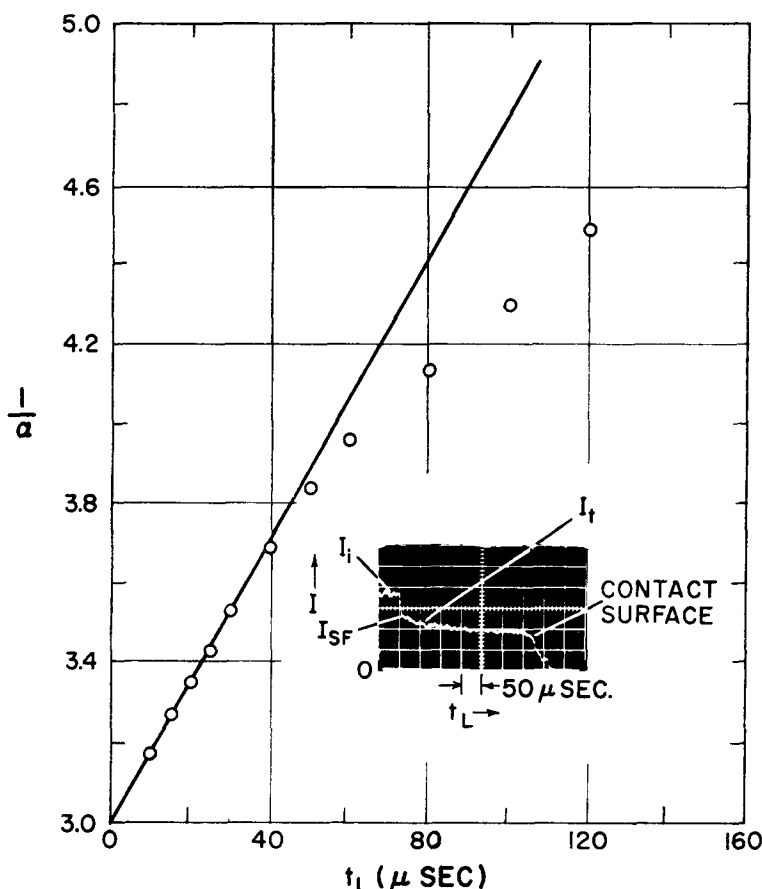
FIG. 6. Typical oscillogram record obtained in the O atom recombination experiment and the plot of $1/\alpha$ against laboratory time obtained from it. Shock conditions: 0.5% O_3–99.5% Ar, $P_1 = 40$ cm, $U_s = 1.545$ mm/μsec, $T_2 = 2400°$K.

curves shown in Fig. 7, identified by authors' names.[1,2,7,10,11] The T^{-n} indicated after each name gives the pre-exponential temperature dependence assigned to the dissociation rate constant. The thickened portion of the curve represents the temperature range over which the data were actually obtained while the thin portion of the curve follows the analytical expression given by the various workers. It is to be noted that the single analytical expression given in Eq. (8) for the dissociation rate adequately fits the recombination data obtained in the experiment here described and was indeed the basis for the $T^{-\frac{1}{2}}$ pre-exponential factor. Thus, at least for the O_2–Ar system, the relationship $K_{eq} = k_d/k_r$ is valid within the accuracy of the experiments used to independently determine k_d and k_r.

Details of the Shock Front

The motivation for carrying out this portion of the experimental program was to ascertain whether or not rotational equilibration occurred simultaneously with the translational equilibration and, furthermore, to establish whether processes such as vibrational relaxation and dissociation commenced before the completion of translational and rotational equilibrium. A Mach Number range of from 4–21 in pure O_2 was covered.

Because of the high resolution required in this experiment, the work was carried out in the 24-in. shock tube at pressures of 15 μ Hg and 30 μ Hg. In order to reduce shock front curvature effects the knife-edge technique was employed utilizing a 4-in. optical path between knife edges. Hence, for this geometry, $\delta = \delta_0/36$. The slit width used was $\frac{1}{2}$ mm and thus, for $P_1 = 15$ μ Hg and $U_s = 1.4$ mm/μsec (the lowest shock speed), the curvature thickness from Eq. (4) is $\delta = 0.4$ mm. From Eq. (6) we find $\tau_{res} = 0.6$ μsec which was a small fraction of the relaxation time being studied.
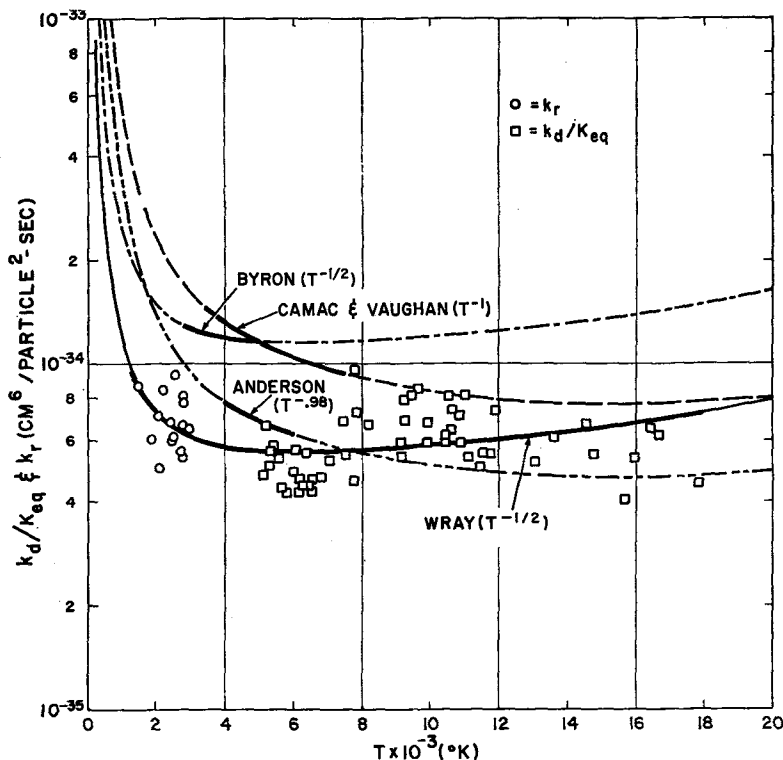
FIG. 7. The recombination rate constants and the previously obtained dissociation rate constants divided by the equilibrium constant, both plotted against temperature. The curves are obtained by dividing the dissociation rate constants (given by various workers) by the equilibrium constant. The temperature dependencies indicated are for k_d. The heavy solid portion of each curve indicates the temperature range over which the data were actually obtained.

In Fig. 8 is shown an oscillogram record of a low Mach Number run along with the density plot made from it. The density ratio is obtained via the equation

$$I/I_1 = \exp\{-l(P_1/P_0)(T_0/T_1)$$

$$\times[(\rho/\rho_1)k(T_v) - 315]\}. \quad (12)$$

This equation is readily derivable from Eq. (1), where I is the light transmitted at any time and I_1 is the light intensity before shock arrival. The number 315 is the absorption coefficient for vibrationally unexcited O_2 while $k(T_v)$ is obtained from Fig. 2, $\lambda = 1470$ Å. To find ρ/ρ_1 from this equation one must establish the vibrational temperature at the time corresponding to the density ρ in order to put in the correct $k(T_v)$. In constructing the density plot from the oscillogram shown in Fig. 8 T_v was assumed to be $300°K$, so that $k(T_v) = 315$. The density profile shown in Fig. 8 exhibits the S-shape typical of all of the density profiles obtained.

The maximum slope shock front thickness L

was determined graphically from these profiles according to the definition

$$L = (\rho_2 - \rho_1)/(d\rho/dx)_{max}$$

$$= (\rho_2 - \rho_1)U_s/(d\rho/dt_L)_{max}, \quad (13)$$

where x is the distance behind the shock front.

These shock front thicknesses were normalized by the mean free path ahead of the shock l_1. At $T_1 = 300°K$ and $P_1 = 15\ \mu$ Hg, $l_1 = 3.58$ mm. In Fig. 9 the normalized reciprocal shock thickness is plotted against the shock Mach Number. The dashed curve is a subjective fit to the data. It is seen that the shock front thickness decreases from 3 ambient mean free paths at $M_s = 4$, to 2 ambient mean free paths at Mach 10 and remains essentially constant at higher Mach Numbers. Also shown in this figure is a theoretical curve due to Mott–Smith[12] whose theoretical model employed a bimodal temperature distribution and an infinitely fast rotational relaxation rate.

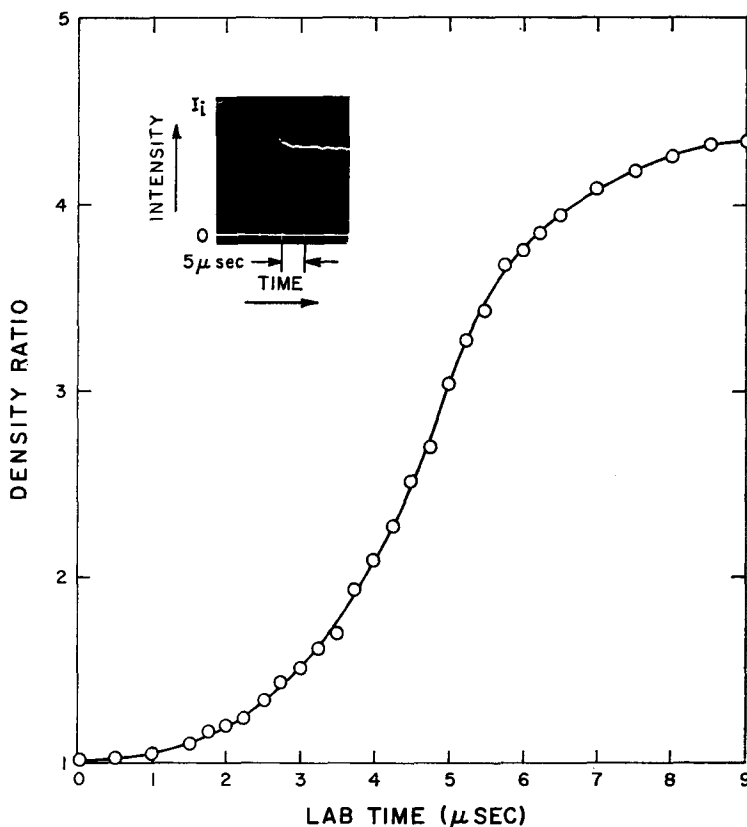Between Mach 4 and Mach 10 the oscillogram

FIG. 8. The density ratio plotted against laboratory time through the O_2 shock front. The inset shows the oscillogram from which these data were obtained. Only the early portion of the time history is recorded. The density profile exhibits the symmetrical S-shape typical of all the profiles obtained. Shock conditions: $M_s = 4.2$, $P_1 = 30~\mu$ of Hg, $T_{trans-rot} = 1300°K$.

traces look essentially like that shown in the inset in Fig. 8. However, above Mach 10 the situation becomes somewhat more complex.[3] Oscillograms between Mach 10 and Mach 14 display a maximum in the absorption near the end of the shock front. This phenomenon is observed only between Mach 10 and 14, and is interpreted as the onset of vibrational relaxation. Above Mach 16 the smaller change in absorption is interpreted as the onset of chemical relaxation within the shock front. The highest Mach Number run made, $M_s = 20.7$, clearly indicates that dissociation has begun within the "shock front."

The qualitative statements concerning the shock front made in the previous paragraph can be made quantitative by computing the density ratio across the "shock front." This can be done via Eq. (12) providing we know the vibrational temperature which supplies the $k(T_v)$. In Fig. 10 we have plotted the density ratio across the

"shock front" as a function of Mach Number. Each run yields two data points assuming (i) vibration is unexcited so that $k(T_v) = 315$ cm^{-1} and, (ii) vibration has gone to local equilibrium and $k(T_v)$ is obtained from Fig. 2 ($\lambda = 1470$ Å). Also shown in Fig. 13 are three theoretical curves calculated from the shock conservation equations assuming: 1, translational relaxation only; 2, translational and rotational relaxation; and 3, translational, rotational, and vibrational relaxation. These curves do *not* necessarily represent actual states of the gas but rather the situation that would exist if the relaxation times were such that $\tau_{trans} \ll \tau_{rot} \ll \tau_{vib} \ll \tau_{dissoc}$.

Inspection of Fig. 10 indicates that between Mach 4 and Mach 10 the data points, computed assuming no vibrational relaxation, scatter about the translation + rotation curves, whereas above Mach 10 these data points fall below this curve and, indeed, eventually fall below the transla-
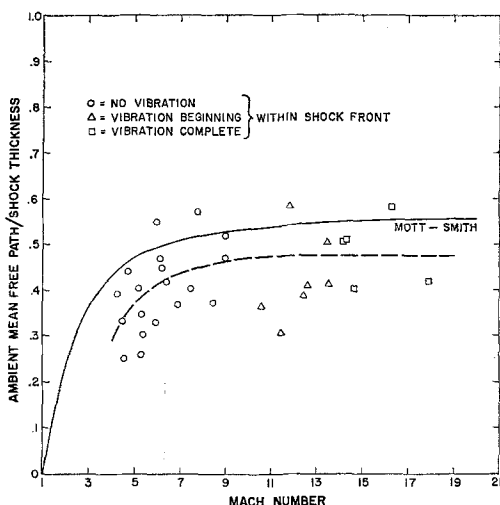
FIG. 9. Reciprocal shock thickness normalized with respect to the ambient mean free path plotted against shock Mach Number. The dashed curve is a subjective fit to the data. The solid curve is based on a theoretical model due to Mott-Smith.

tional curve. On the other hand, the data points between Mach 4 and Mach 10, computed assuming complete vibrational relaxation, are nonsensical simply because vibration is not complete in this regime. Between about Mach 10 and 16, the data points interpreted in this manner scatter about the translational + rotational + vibrational equilibrium curve; above Mach 16, the data points again fall off in a meaningless manner. This is due to the fact that chemical dissociation has commenced. In Fig. 10, the blackened data points are those which were computed using the absorption coefficient appropriate to the vibrational state of the gas just behind the "shock front."

Comparison with Other Data and Conclusions

In order to compare the efficiencies of the catalysts Ar, O_2, and O in dissociating O_2 and to determine the extent of agreement for the same catalyst, we have plotted the results of several investigations[1,2,7,10,11,13—15] in Fig. 11.
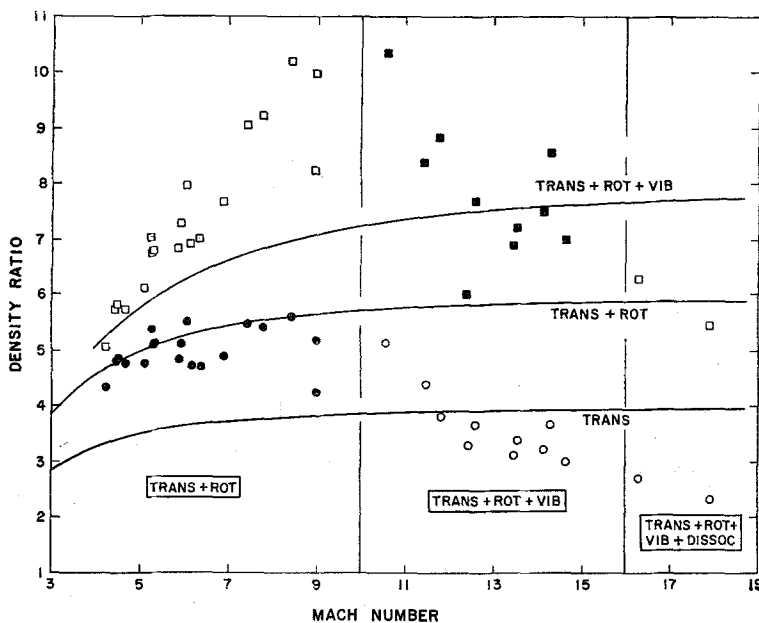

FIG. 10. The density ratio across the "shock front" plotted against shock Mach Number. Two data points were computed for each run assuming: (i) no vibrational relaxation had occurred (O); (ii) vibrational relaxation had gone to completion (□). The three theoretical curves were calculated from the shock conservation equations. The data are divided into three regimes corresponding to the processes which are occurring at the "shock front," the correctly computed data points being blackened.
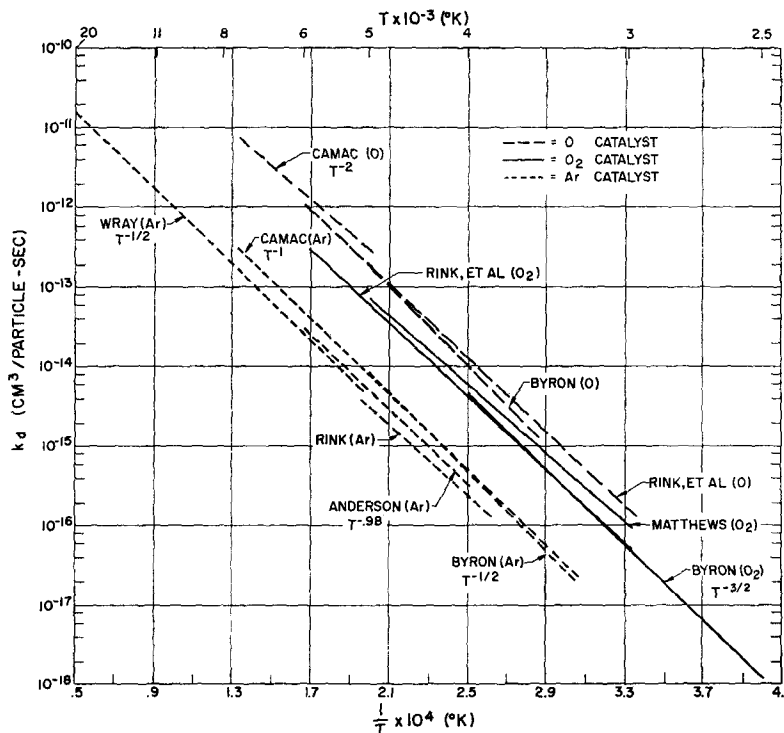
FIG. 11. Survey of the dissociation rate constant for the catalysts Ar, O_2, and O obtained by various workers. The analytical results given by the authors are plotted here only over the experimental range given in the publication. A pre-exponential temperature dependence is indicated only where the authors claimed that the T^{-n} was deduced from their data.

These curves were computed from the analytic expressions given by the authors and they are plotted here over the specified range of validity. Where the author claimed that a pre-exponential temperature dependence was *deduced from the data*, it is indicated in Fig. 11; where it was guessed or theorized, it is not given in the figure. Notice that for O only Camac and Vaughan,[7] and for O_2 only Byron[11] have claimed measurement of T^{-n}. For Ar Wray[1,2] and Byron[11] claim $T^{-\frac{1}{2}}$, and Camac and Vaughan[7] and Anderson[10] claim T^{-1}.

That the catalysts differ in efficiency is undoubtedly true, though their ratios are somewhat uncertain. Using the lower k_d results for Ar (Wray,[1] Rink,[14] and Anderson[10]) it is estimated that $Ar:O_2:O = 1:18:50$ over a fairly wide temperature range. If the higher Ar results (Camac and Vaughan,[7] and Byron[11]) were taken, $1:9:25$ is estimated.

In Fig. 12 are plotted the measured relaxation times (at STP density) for the various phenomena occurring in shocked O_2 or O_2-Ar mixtures. Extrapolated portions of the curves are

dashed. The time for translational–rotational relaxation to occur under experimental conditions is taken as the shock thickness (dashed curve, Fig. 9) divided by the shock speed. For this case only, the temperature given by the abscissa in Fig. 12 is the temperature *after* translational and rotational relaxation. Some of the uncertainties in the dissociation rate constants exhibited in Fig. 11 have been "averaged out" so as not to cloud the main point to be made by examining this figure, i.e., at high temperatures these processes all tend to converge to a common relaxation time. It is nonsensical to have the Vib(O_2) curve cross the trans + rot curve which it does at 12,000°K (∼Mach 14). In fact the shock front study indicated that by Mach 10 ($T \sim 6000$°K), the vibrational relaxation process was beginning to be swallowed by the translational–rotational process. The same is to be said for the dissociation processes although they do not enter this regime until slightly higher Mach Numbers. It would seem that experimental and theoretical investigations of this regime—where vibrational and dissociative processes are
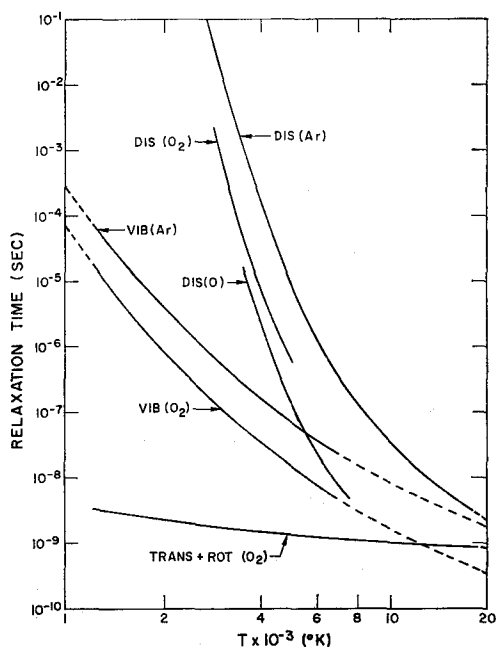
FIG. 12. Relaxation times at a density corresponding to 1 atm and 273°K plotted against temperature for the various processes occurring in shock heated O_2 or O_2–Ar mixtures. Note how all the processes tend to converge to a common relaxation time at very high temperatures.

occurring in a gas not yet characterized by a Boltzmann distribution of translational and rotational energies—would be most interesting.

It is, of course, also of great interest to extrapolate the high-temperature shock tube measurements to room temperature and compare them with recombination data taken by completely different techniques. Doing this also allows comparison to be made between the relative efficiencies of various catalysts at high and low temperatures. The literature appears to contain substantial discrepancies between the efficiencies of various catalysts measured in dissociation experiments in the shock tube as opposed to recombination experiments in the vicinity of room temperature. In Fig. 13 are plotted the recombination coefficients resulting from several low temperature investigations, some shock tube recombination data obtained at intermediate temperatures (1500°–3000°K), and extrapolated recombination rate constant curves obtained by dividing the shock tube dissociation rate constant by the equilibrium constant. Some of this information is summarized in Table I.

The only low temperature oxygen recombination experiment where Ar serves as a catalyst

appears to be that due to Morgan and Schiff.[16] They prepared their O atoms by reacting N atoms with NO, which yielded a dilute O–N_2 mixture ($O/N_2 \approx 1/200$), and hence they measured the recombination rate for N_2 catalysts recombining O atoms. By adding other gases, they were able to evaluate the recombination rates of five other catalysts including Ar. Addition of up to 41 mole-% Ar showed *no* increase of recombination rate, and all that could be obtained was an upper limit to the rate constant of 9×10^{-34} which is indicated in Fig. 13.

The study of Reeves et al.[17] is shown in Fig. 13 with a question mark for the catalyst(s) involved. They worked with 5%–20% O_2 in Ar mixtures, with large fractions of the O_2 dissociated by electric discharges ($O/Ar \approx 1/15$). These workers claim a recombination rate of 2.7×10^{-33} independent of the catalyst. *If* the O atom has a significantly higher efficiency in recombining O atoms at room temperature, it should become apparent in these experiments. Unfortunately, these workers took O concentra-
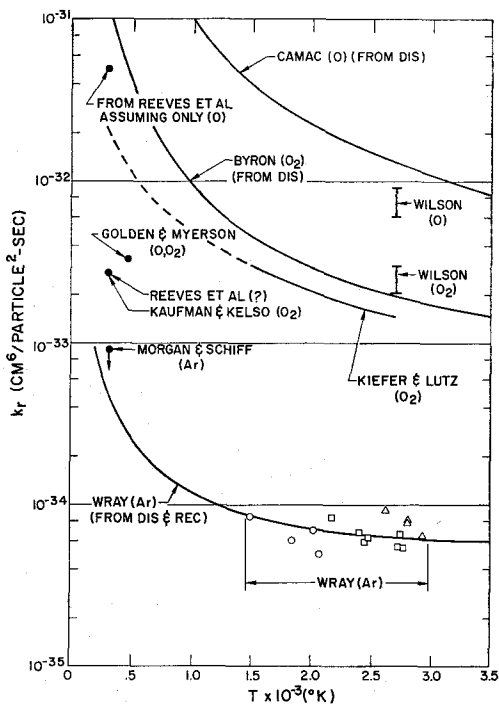

FIG. 13. A comparison of the room temperature recombination coefficients for oxygen by various catalysts with the recombination coefficients measured directly in shock tube experiments (1500°K < T < 3000°K), and with extrapolated high temperature dissociation rate constant measurements divided by the equilibrium constant.

TABLE I

Rate constant expression for O_2 dissociation and recombination (cm^6/particle^2·sec)

Cata-lyst	Dissociation rate shock tube measurements	Recombination rate from shock tube measurements, $\lim T \rightarrow 300°K$	Recombination rate from shock tube measurements, $T = 300°K$	Recombination rate room temperature measurements
Ar	$4.2 \times 10^{-8}T^{-\frac{1}{2}}\exp(-D/RT)$ Wray[1,2]	$2.5 \times 10^{-30}T^{-\frac{3}{2}}$	4.8×10^{-34}	$<9 \times 10^{-34}$ Morgan and Schiff[16]
				2.7×10^{-33} Reeves et al.[17]
O_2	$3.2 \times 10^{-3}T^{-\frac{3}{2}}\exp(-D/RT)$ Byron[11]	$1.9 \times 10^{-25}T^{-\frac{5}{2}}$	1.3×10^{-31}	2.7×20^{-33} Kaufman and Kelso[18]
				3.3×10^{-33} Golden and Myerson[19]
O	$1.1 \times 10^{0} \times T^{-2}\exp(-D/RT)$ Camac and Vaughan[7]	$6.5 \times 10^{-23}T^{-3}$	2.5×10^{-30} Camac and Vaughan[7]	$\sim5 \times 10^{-32}$ Wray, from the data of Reeves et al.
			3.9×10^{-31} Average extrapolated	3.3×10^{-33} Golden and Myerson[19]

tion information at only two positions in the flow tube (corresponding to 2 times), so that the mechanism cannot be deduced from the data. However, if it is *assumed* that the O atom is the dominant catalyst in Reeves' work, the data lead to a recombination coefficient of about 5×10^{-32} with little more scatter in the results than presented in their analysis which assigns all catalysts the same efficiency. A more detailed analysis of their data in this light is probably not justified since there is some question concerning the rate of wall recombination in their experiments.

In the work of Kaufman and Kelso[18] (a flow tube discharge experiment) the O_2 molecule should dominate as the catalyst

$$(\tfrac{1}{100} < O/O_2 < \tfrac{1}{7}).$$

Golden and Myerson[19] used a static system (discharge turned off at time zero) and followed the O_2 concentration as a function of time by flash spectroscopy in the Schumann–Runge system. The fraction of O_2 dissociated in their experiments was very high and yet they found $k_r = 3.3 \times 10^{-33}$ independent of catalyst.

There is the question of the effect of the $^1\Delta_g O_2$ in all these room temperature experiments where the O atoms are prepared by discharge as has been pointed out by Kaufman.[18]

The work of Wilson[20] is indicated at a single

temperature of 2700°K. This was a shock tube experiment in which the partially dissociated O_2 behind the incident shock front was cooled by expansion of the shocked gas over an air foil. The dominant catalysts in this experiment were O_2 and O. Wilson *assumed* $k_O/k_{O_2} = 3$ in his data analysis. If he had assumed a smaller ratio of catalytic efficiencies, his resultant recombination rate for O_2 would increase and vice versa.[21]

The curve due to Kiefer and Lutz[22,23] was obtained in an experiment very similar to the O_3 technique outlined above except these workers used high concentrations of O_3 and measured the density behind the shock as a function of time by absorption of x-rays. The recombination rates were measured after the O atom concentration had decreased to a point where the dominant catalyst should be O_2.

It is frequently argued that it is improper to compute recombination rates from shock tube measurements of dissociation rates. However, this argument does not seem to be borne out experimentally if the shock tube dissociation and recombination data are compared. The use of such an argument to explain away apparent disagreement between room temperature recombination rates and those extrapolated from shock tube dissociation measurements as has been suggested by several workers[16,18] seems unjustifiable.

In the case of Ar, the agreement between the

high and low temperature studies is good. The
temperature dependence (see Table I) for re-
combination in the vicinity of 300°K is $T^{-3/2}$. In
the case of O and O_2 catalysts, however, extrapo-
lated high temperature measurements are sig-
nificantly higher than measurements at room
temperature indicate—even when the data are
reinterpreted to assign high catalytic efficiency
to the O atom. These apparent discrepancies
can be explained in three possible ways: 1, the
shock tube measurements are incorrect; 2, the
room temperature measurements are incorrect;
or 3, both are correct and the temperature de-
pendence changes significantly between 300°
and 3000°K. The latter of these three possibilities
seems to have best chance of being correct. Good
measurements of O recombination between 300°
and 3000°K for O and O_2 catalysts would be of
great interest and should be made.

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    The curve of Kiefer and Lutz, shown in Fig. 13,
    is the result of more recent experiments than
    those presented in Ref. 22. They have been sub-
    mitted for publication in J. Chem. Phys.

COMMENTS

Prof. S. H. Bauer (Cornell University): It is worth
mentioning that the "incubation time" which Wray
found can be accounted for by a semiempirical
analysis (which is based on a very plausible model)
developed by Treanor at the Cornell Aeronautical
Laboratory. The point hinges on the departure from
vibrational equilibrium populations in the upper-
most vibrational levels, due to the fact that when
dissociation occurs, depopulation of these levels by
recombination (three-body process) is much less
than the rate of depopulation by dissociation during
the early stages of the process. Under these condi-
tions, there is really no defined vibrational tempera-
ture. The approximate description of the relative
population by some average temperature becomes
worse as the shock temperature is raised. To the
extent that such an approximate description is given,
it appears that (T_v) is less than T_{trans} and T_{rot} for a
much longer time than τ_v.

At the very high temperatures, at which Dr. Wray

found a near-coalescence of the relaxation times for
dissociation and vibration, the ΔT must be apprecia-
ble, and one is forced to assume that most dissocia-
tions occur from the lower vibrational states by
means of single energetic collisions. The detailed
mechanics for such a process has not yet been
analyzed. Indeed, it is a difficult molecular process
to describe accurately.
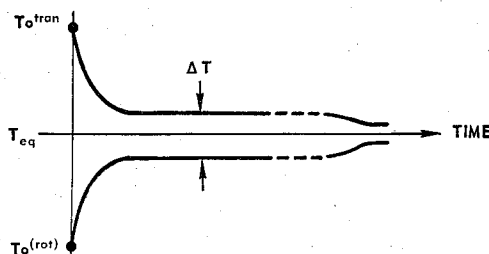
Dr. K. L. Wray: It is true that Treanor was able to fit the experimental incubation times with his coupled vibration–dissociation model. It should, however, be pointed out (without detracting from this accomplishment) that his semiempirical model assumes an exponential probability of dissociation from the various vibrational levels. This requires introduction of a parameter which describes how rapidly the dissociation probability drops off for low vibrational levels, and the experimental data were fitted by adjusting this parameter.

♦

Prof. A. R. Ubbelohde (Imperial College): In view of the accurate information becoming available about energy terms and rate constants for various elementary reactions, it seems timely to refocus attention on "abnormal" pre-exponential factors in the various rate equations proposed. Too little has been said about this aspect of the data in the present symposium.

For example, in the three reactions proposed by Wray

$$O_3 + Ar \rightarrow O + O_2 + Ar \qquad (1)$$

$$O + O_3 \rightarrow 2\ O_2 \qquad (2)$$

$$O + O + Ar \rightarrow O_2 + Ar, \qquad (3)$$
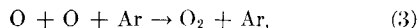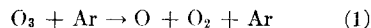
at a guess, it might be anticipated that Reaction (3) has a smaller steric factor $\theta/2\pi$, where θ is the solid angle within which collision trajectories must lie for effective bond rearrangement, than either Reactions (1) or (2). But there are rather subtle possibilities which could make a crude guess far from matching the actual pre-exponential factors in these three reactions. In particular, marked anisotropy in intermolecular force fields may be found for some of these collisions. This, in itself, can distort energy-transfer-rate equations for transfer of internal energy, to an extent we still need to map out.