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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE RATE OF DISSOCIATION OF OXYGEN MOLECULES AT HIGH TEMPERATURES

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The study of processes of interaction between molecules that lead to their decomposition has become timely in connection with consideration of problems concerning the state of a gas at high temperatures developing behind the front of a strong shock wave. In a number of works the rate of decomposition of such molecules as O_2, Br_2, J_2 has been measured; the dissociation of both pure gases and mixtures with inert and other diluents has been investigated ([1]).

Seeking to obtain results over a wider temperature range, we attempted to measure the rate of decomposition of O_2 molecules at temperatures up to 7000°. The experimental method is based on an earlier study of this phenomenon at lower temperatures ([2]); the main idea of the method, which made it possible to carry out measurements at such high temperature values, is to investigate the dissociation process at its very beginning, when the energy losses for dissociation and the associated decrease in temperature are still small. The investigations were carried out in a shock tube; the main data on the apparatus used are given in ([3]).

Fig. 1. Distribution of the absorptivity A (1), temperature T (2), and concentration of molecular oxygen ξ_{O_2} (mole fraction of O_2) (3) behind the front of a shock wave propagating in oxygen with a velocity of 4.1 km/sec. $\bar{T}$ and $\bar{\xi}$ are the equilibrium values of temperature and concentration. Φ is the position of the shock-wave front. Pressure 0.11 atm. Time is laboratory time.

In the experiments, the distribution of the absorptivity (Fig. 1, 1) behind the front of a strong shock wave ($\lambda = 2275$ Å) was measured with high time resolution (0.025 μsec). Since, in the selected portion of the spectrum, light is absorbed only by vibrationally excited O_2 molecules ($v'' \sim 4.5$), the appearance of absorption can be associated with the process of excitation of the initial levels, and the decrease in absorption with the process of dissociation. The

dependence of the absorptivity A on the concentration n_{O_2} of oxygen molecules per unit volume and on the temperature T was obtained by measuring A in the equilibrium region at a sufficient distance from the leading front of the shock wave and at the point of maximum absorption—during the transition from the region of vibrational excitation to the region of dissociation. The first measurements made it possible to determine $A(T, n_{O_2})$ for $T < 3000 \div 4000°$; extrapolation of these results to higher T in accordance with the Boltzmann distribution law over the initial vibrational levels agrees, within the accuracy of measurement,

with the values of A measured at point m (Fig. 1) for T up to 7000° K, if it is assumed that at this point the relaxation of the vibrational energy has ended, while appreciable dissociation has not begun.* Strictly speaking, this assumption is not valid (especially for high temperatures): near point m the processes of vibrational relaxation and nonequilibrium dissociation overlap. However, the character of the dependence of A on T indicates that this overlap at $T_m \sim 5000 \div 7000°$ cannot substantially affect the value of the absorptivity. It was established that for $A \leqslant 0.2 \div 0.3$ the absorptivity is proportional (under conditions of vibrational equilibrium) to the concentration n_{O2}, i.e.

$$A = n_{O2}\varphi(T), \tag{1}$$

where $\varphi(T)$ is the obtained temperature dependence. Using the relation between n_{O2} and T that follows from the law of conservation of energy,

$$n_{O2} = p\,\frac{\dfrac{D}{2kT} + \dfrac{5}{2} - \dfrac{mV^2}{4kT}\left[1 - \left(\dfrac{\rho_0}{\rho}\right)^2\right]}{\dfrac{D}{2} + \dfrac{5}{2}kT + \dfrac{mV^2}{4}\left[1 - \left(\dfrac{\rho_0}{\rho}\right)^2\right] - h(T)}, \tag{2}$$

(where D is the dissociation energy; k is the Boltzmann constant; m and $h(T)$ are the mass and enthalpy of an oxygen molecule; V is the wave velocity; p and ρ are the gas pressure and density behind the wave front; ρ_0 is the density ahead of the wave), one can eliminate n_{O2} from (1). Since the second term in square brackets is less than 0.015, its change may be neglected by taking the mean value for ρ/ρ_0. The pressure p, as is known, changes only slightly in the nonequilibrium region; it may likewise be approximated by a mean value. Then from (1) and (2) one obtains a relation between the temperature T, the measured values of the shock-wave velocity V, and the absorptivity A; this makes it possible to obtain the distribution of T behind the wave front in the dissociation zone (Figs. 1, 2) and, passing to mole fractions $\xi_{O2} = n_{O2}(kT/p)$, the distribution of ξ_{O2} (Figs. 1, 3).

Fig. 2. Values of the logarithm of the rate constant for decomposition of oxygen molecules (dimension K cm^3/(mol · sec)). Dashed lines: 1 —according

to [2], 2 –according to [8], 3 –according to [5].

Then, neglecting the possibility of recombination (which, apparently, is possible for states sufficiently far from complete equilibrium), for the change of ξ_{O2} behind the shock-wave front we obtain

$$\frac{d\xi_{O2}}{dt} = -(1+\xi_{O2})\frac{p}{kT}\left[K_d(O_2,O_2)\,\xi_{O2}^2 + K_d(O_2,O)\,\xi_{O2}(1-\xi_{O2})\right], \quad (3)$$

where $K_d(O_2,O_2)$ and $K_d(O_2,O)$ are the rate constants for decomposition of O_2 molecules in O_2-O_2 and O_2-O collisions, respectively. Using for $K_d(O_2,O)$ the values obtained in [4,5], from (3) we find $K_d(O_2,O_2)$. The experiments carried out made it possible to obtain values of $K_d(O_2,O_2)$ at temperatures 4000-7000° K. The range of obtained values is hatched in Fig. 2; the solid line gives the mean value of $K_d(O_2,O_2)$. The presence of a significant scatter is associated with measurement errors (finite thickness of the oscillographic beam, photomultiplier noise, etc.).

*

* The temperature T and other characteristics of the gas state were calculated according to the conservation laws of mass, momentum, and energy, taking into account the equation of state in accordance with the known conditions ahead of the shock wave and the measured (with an accuracy of 1-2%) wave velocity.

Let us represent K_d in the form of the Arrhenius relation $K_d = PZ\exp\{-(D/kT)\}$, where Z is the number of collisions per unit volume per second, calculated per one molecule. It is usually assumed that the temperature dependence of the preexponential factor P is determined mainly by the factor $(D/kT)^n$. According to [6,7], for collisions of diatomic molecules with monatomic particles the value of n is close to 1.5. For O_2—Ar collisions this agrees well with the experiments of Kamac and Vaughan [4]. For O_2—O_2 collisions Matthews [8] found that in the range $2400 \div 4600$°K, $n = 3$. For our results n approaches 4. One possible explanation for such a strong dependence of P on T, as indicated in [4], is the absence, at high temperatures, of complete vibrational equilibrium. The incompleteness of vibrational relaxation by the onset of dissociation apparently sets a limit on the possibility of determining, by means of shock waves, the value of the decay-rate constant as a single-valued function of temperature: with increasing shock-wave velocity (and temperature), the value of K_d will depend not only on temperature, but also on the time after passage of the shock front. For the entire temperature range studied, from 2400 to 7000°K, the value $K_d(O_2,O_2)$ can, within the scatter of the results, be interpolated by the relation

Fig. 3. Average values of the preexponential factor P in the expression for the decay-rate constant as a function of $(D/kT)^3$ for collisions O_2—O_2 (1, 2, 3) and

Figure 3: Average values of the preexponential factor P in the expression for the decay-rate constant as a function of $(D/kT)^3$ for O_2—O_2 collisions (1, 2, 3) and O_2—Ar (4). 1—results of the present work; 2—Matthews' data [8]; 3—Bayron' s data [5]; 4—Kamac and Vaughan' s data [4].

Figure 2: Figure 3: Average values of the preexponential factor P in the expression for the decay-rate constant as a function of $(D/kT)^3$ for O_2—O_2 collisions (1, 2, 3) and O_2—Ar (4). 1—results of the present work; 2—Matthews' data [8]; 3—Bayron' s data [5]; 4—Kamac and Vaughan' s data [4].

O_2—Ar (4). 1—results of the present work; 2—Matthews' data [8]; 3—Bayron' s data [5]; 4—Kamac and Vaughan' s data [4].

$$K_{\mathrm{d}}(\mathrm{O}_2, \mathrm{O}_2) = 2 \cdot 10^{-2} \left(\frac{D}{kT}\right)^3 Z \exp\left\{-\left(\frac{D}{kT}\right)\right\}, \tag{4}$$

however, extrapolation of such a relation to higher values of T should be carried out with caution.

Comparison of the values of P for O_2—O_2 and O_2—Ar collisions makes it possible to reveal the difference between the mechanism of interaction in collisions of a dissociating molecule with particles having different structure. For this purpose Fig. 3 presents the values $P(\mathrm{O}_2, \mathrm{O}_2)$ and $P(\mathrm{O}_2, \mathrm{Ar})$ as functions of $(D/kT)^3$. It follows from Fig. 3 that the ratio $\alpha = P(\mathrm{O}_2, \mathrm{O}_2)/P(\mathrm{O}_2, \mathrm{Ar})$ decreases significantly with increasing temperature (from $\alpha \sim 30$—40 at $T = 3500°\mathrm{K}$ to $\alpha \sim 5$—10 at $T = 7000°\mathrm{K}$). According to E. E. Nikitin [9], taking into account the transfer of rotational energy in O_2—O_2 collisions gives the value $\alpha \sim 20$, independent of temperature. The character of the obtained values of P indicates the need for further refinement of the picture of the process.

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Note: Figure translations are in progress. See original paper for figures.