DISSOCIATION OF OXYGEN MOLECULES IN COLLISIONS

1969

SovietRxiv

Abstract

Full Text

UDC 536.45

PHYSICS

S. A. LOSEV, O. P. SHATALOV

DISSOCIATION OF OXYGEN MOLECULES IN COLLISIONS

O_2–O_2 AND O_2–O

(Presented by Academician V. N. Kondrat’ev, 16 VII 1968)

In a number of works, a high efficiency of dissociated O atoms and O_2 molecules in the dissociation of O_2 at temperatures of 3000-7000° was noted, as compared with the efficiency of the argon atom (^{1}-^{3}). Values of the dissociation rate constants $k(O_2-O)$ and $k(O_2-O_2)$ at higher temperatures are usually obtained by extrapolating dependences obtained at $T \leqslant 7000^\circ$ (^{4}-^{6}). However, such extrapolation cannot always be considered satisfactory. Indeed, at $T > 10\,000^\circ$K the extrapolated characteristic dissociation time of O_2 in collisions with O becomes less than the molecular mean free time, which is meaningless.

To clarify this question, experiments were carried out in a shock tube. The shock wave propagated in a mixture of 10% O_2 + 90% Ar. The concentration of molecular oxygen in the gas behind the shock-wave front was measured by an absorption spectroscopic method, analogous to that described in (^{3}), but in the far quartz and vacuum ultraviolet regions of the spectrum (absorption in the continuum and in the bands of the Schumann–Runge system of O_2).

Samples of the oscillograms obtained in the experiments are shown in Fig. 1. As the earlier analysis showed (see (^{3}, ^{6})), behind the shock-wave front there is a drop in the signal associated with excitation of molecular vibrations. In experiments at $\lambda \leqslant 1700$ Å, the signal decreases stepwise at the shock-wave front owing to an increase in the gas density (in this case the cold gas ahead of the wave absorbs light). In all cases (with sufficiently strong shock waves), this is then followed by an increase in the signal (a decrease in absorption) associated with dissociation of the molecules. At complete dissociation, the signal level is restored to that observed in the absence of absorbing gas in the low-pressure chamber of the shock tube.

Fig. 1. Samples of the recorded absorption traces of radiation behind the shock-wave front. Top –$\lambda = 1640$ Å, $V = 2.96$ km/sec, $p_1 = 7$ torr; bottom – $\lambda = 1850$ Å, $V = 2.94$ km/sec, $p_1 = 6.6$ torr (time marks 0.5 μsec).

Fig. 1. Samples of the recorded absorption traces of radiation behind the shock-wave front. Top $-\lambda = 1640$ Å, $V = 2.96$ km/sec, $p_1 = 7$ torr; bottom $-\lambda = 1850$ Å, $V = 2.94$ km/sec, $p_1 = 6.6$ torr (time marks 0.5 μsec)

Figure 1: Fig. 1. Samples of the recorded absorption traces of radiation behind the shock-wave front. Top $-\lambda = 1640$ Å, $V = 2.96$ km/sec, $p_1 = 7$ torr; bottom $-\lambda = 1850$ Å, $V = 2.94$ km/sec, $p_1 = 6.6$ torr (time marks 0.5 μsec)

A study of the dependence of the absorptivity A of molecular oxygen at temperatures 3000–10 000° indicated that Beer' s law is obeyed,

$$A = 1 - \exp\left[-\gamma_{O2} n_1 \frac{\rho}{\rho_1} p_1 \sigma(T)\right], \tag{1}$$

where γ_{O2} is the concentration of O_2 molecules (^{7}), $\sigma(T)$ is the effective absorption cross section, n_1 is the number density of all particles ahead of the wave, and ρ_1, ρ are the dens–

of the gas before the front and in the flow behind the shock-wave front, p_1 is the initial gas pressure.

Thus, the absorptivity in the zone of nonequilibrium dissociation behind the shock-wave front depends on the concentration γ_{O2}, the gas density ρ, and the temperature T.

In an $O_2 + Ar$ mixture at high temperatures one may assume the existence of three paths of oxygen dissociation: in collisions of an O_2 molecule with O_2, O, and Ar. Then, taking the recombination process into account, it is not difficult to arrive at a kinetic equation for the concentration of O_2 in a form convenient for use in machine computation (see (7)):

$$\frac{d\gamma_{O2}}{dt} = p_1 \left(\frac{\rho}{\rho_1}\right)^2 k^{\mathrm{Ar}} \left(4.492 \cdot 10^{-6} p_1 \rho \gamma_{O}^2 \frac{T}{K_{O2}} - \gamma_{O2}\right) \left(\alpha_{O2}\gamma_{O2} + \alpha_O \gamma_O + \gamma_{\mathrm{Ar}}\right), \tag{2}$$

where k^{Ar} is the reduced rate constant of oxygen dissociation in O_2–Ar collisions*, p_1 is the initial gas pressure before the shock wave (in torr); K_{O2} is the equilibrium constant (in atm.); α_{O2} and α_O are the relative efficiencies of oxygen molecules and atoms in dissociation (relative to the efficiency of an argon atom). The concentration of atomic oxygen is then found from the relation

$$\gamma_O = 2[(\gamma_{O2})_0 - \gamma_{O2}], \tag{3}$$

where $(\gamma_{O2})_0$ is the initial value of γ_{O2}, while the argon concentration γ_{Ar} remains constant (we neglect argon ionization and other processes).

The quantities T and ρ can be found on the basis of the conservation laws for the fluxes of mass, momentum, and energy, and the equation of state (6).

The method of solving the problem is as follows. For the constant k^{Ar} the value known from experiments (8) is used, and trial values are taken for the quantities α_{O2} and α_{O}. Next, numerical integration of equation (2) is carried out (by Euler' s method on an electronic computer), and the values of γ_{O}, T, ρ, and A are calculated simultaneously. The calculated absorptivity A is compared with the experimental trace, and the problem is solved in the next approximation with respect to the quantities α_{O2} and α_{O}. Both quantities can be obtained from a single experiment, since O_2—O_2 collisions make an appreciable contribution to $A(t)$ only at the beginning of the dissociation process, whereas O_2—O collisions do so only after a sufficient number of oxygen atoms has been formed. The use of an electronic computer makes it possible to make the convergence procedure sufficiently rapid. In this way the processes were considered over the whole dissociation zone up to the establishment of complete equilibrium.

As a result of the processing of the oscillograms, it was found that the relative efficiency of O and O_2 in oxygen dissociation decreases markedly with increasing temperature, approaching the efficiency of argon at $T = 9000 \div 10\,000$°K. In Figs. 2 and 3 the hatched region indicates the values of the constants $k(O_2—O_2)$ and $k(O_2—O)$ measured in the present work, and the solid line gives the mean values. The root-mean-square error in measuring the constants is 60%.

The results obtained lead to a considerable negative dependence of the preexponential factor in the expression $k = B(D/RT)^n \exp(-D/RT)$, where D is the dissociation energy ($n \geq 7 \div 9$). Such a form of the dependence cannot, however, be explained by a decrease in the vibrational temperature in high-temperature quasi-stationary dissociation (9), since the question is one of **relative** efficiency in comparison with an argon atom. For the same reason one cannot accept an explanation based on the convergence of the characteristic times of dissociation and vibrational relaxation at high temperatures; the portions of the oscillograms considered here certainly correspond to a period quasi-stationary dissociation. The observed phenomenon is probably connected with a decrease in the role of attractive forces and other features of the intermolecular potential for the $O_2 - O$ complex, and also with a decrease in the role of vibrational-quantum exchange in $O_2 - O_2$ collisions in the case of stronger collisions. Since the large values of the quantity n in the pre-exponential factor, which vary with temperature, have no

Fig. 2. Values of the rate constant for dissociation of O_2 in collisions with an oxygen molecule.

---

* The quantity k^{Ar} is referred to the number of particles before the shock-wave front at pressure p_1 and is expressed on a microsecond scale. In converting from the dimension $\mathrm{cm}^3/\mathrm{mole} \cdot \mathrm{sec}$, the value of the dissociation rate constant should be multiplied by $3.255 \cdot 10^{-10}$ (see (7)).

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

1—results of work (11); 2—results of (1); 3—results of the present work; 4—$k(\mathrm{O_2}-\mathrm{Ar})$ (8).

Fig. 3. Values of the rate constant for dissociation of $\mathrm{O_2}$ in collisions with an oxygen atom.
1—results of work (1); 2—results of work (2); 3—results of the present work; 4—$k(\mathrm{O_2}-\mathrm{Ar})$ (8).

physical meaning, for the time being one must formally choose an approximating dependence of k on T. In doing this, for extrapolating k to the region of temperatures above 10,000° it is expedient to use the results of (8) and to relate $k(\mathrm{O_2}-\mathrm{O})$ and $k(\mathrm{O_2}-\mathrm{O_2})$ to the quantity $k(\mathrm{O_2}-\mathrm{Ar})$, assuming that for $T > 10{,}000^\circ$ the values of all three constants coincide.

Then, for the values of $k(\mathrm{O_2}-\mathrm{O})$ and $k(\mathrm{O_2}-\mathrm{O_2})$ obtained in the present work, one may recommend

$$k(\mathrm{O_2}-\mathrm{O}) = (1 + 108\theta^{-0.58}\exp[-1.7\cdot 10^{-3}\theta^{3.3}])\,k(\mathrm{O_2}-\mathrm{Ar}), \quad \theta > 4,$$

$$k(\mathrm{O_2}-\mathrm{O_2}) = (1 + 600\theta^{-2.3}\exp[-4\cdot 10^{-9}\theta^{9.2}])\,k(\mathrm{O_2}-\mathrm{Ar}), \quad \theta > 3,$$

where $\theta = T^\circ\mathrm{K}/10^3$.

Analogous results were obtained in (10) in a study of hydrogen dissociation in the reaction $\mathrm{H_2} + \mathrm{H} \to 3\mathrm{H}$. The observed phenomenon is apparently typical for the dissociation processes of any diatomic molecules at very high temperatures.

The authors express their deep gratitude to V. N. Kondrat’ ev for his interest in the work and discussions, and to M. S. Yalovik for assistance.

Research Institute of Mechanics,
Moscow State University
named after M. V. Lomonosov

Received
8 VII 1968

CITED LITERATURE

[1] S. R. Byron, *J. Chem. Phys.*, **30**, 1380 (1959).
[2] M. Camac, A. Vaughan, *J. Chem. Phys.*, **34**, 460 (1961).
[3] N. A. Generalov, S. A. Losev, *J. Quant. Spectr. Radiative Transf.*, **6**, 101 (1966).
[4] K. Rey, in the collection *Investigation of Hypersonic Flows*, Moscow, 1964.

[5] S. C. Lin, J. D. Teare, *Phys. Fluids*, **6**, 355 (1963).
[6] E. V. Stupochenko, S. A. Losev, A. I. Osipov, *Relaxation Processes in Shock Waves*, "Nauka," 1965.
[7] S. A. Losev, V. A. Polyanskii, *Izv. Akad. Nauk SSSR, Mekh. Zhidk. i Gaza*, No. 1, 176 (1968).
[8] K. L. Wray, *J. Chem. Phys.*, **37**, 1254 (1962).
[9] N. M. Kuznetsov, *Dokl. Akad. Nauk*, **164**, 1097 (1965).
[10] J. R. Hurle, *Measurement of Hydrogen Atom Recombination Rates Behind Shock Waves*, XI Intern. Sympos. on Combustion, Berkeley, California, 1966.
[11] S. A. Losev, *Dokl. Akad. Nauk*, **141**, 894 (1961).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.