Reports of the Academy of Sciences of the USSR

1958

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1958. Vol. 120, No. 6

PHYSICAL CHEMISTRY

S. A. LOSEV

INVESTIGATION OF THE PROCESS OF OXYGEN DISSOCIATION BEHIND A STRONG SHOCK WAVE

(Presented by Academician V. N. Kondrat’ ev on 7 III 1958)

In the present work an experimental investigation has been carried out of the rate of thermal dissociation behind a strong shock wave in oxygen. The source of the shock waves was a shock tube, the principle of operation of which is described in detail in the literature ([1,2]).

The state of the gas behind the shock wave was studied from the absorption of ultraviolet radiation by oxygen heated, during passage of the shock wave, to temperatures of several thousand degrees. The light source was a krypton lamp GSVL-120; the light passed through the gas under investigation in a certain section of the shock tube and through a quartz monochromator with two exit slits, which selected spectral regions of width $\Delta\lambda = 10$ Å near $\lambda_1 = 2272$ Å and $\lambda_2 = 2510$ Å. The transmitted light then fell on FEU-18 photomultipliers. The signals obtained during passage of the shock wave were recorded on the screen of an OK-17M oscilloscope (Fig. 1).

Fig. 1. Oscillogram of the absorption of ultraviolet radiation during passage of a shock wave in oxygen with a velocity of 3 km/sec. **1** –in the region $\lambda_1 = 2272$ Å; **2** –in the region $\lambda_2 = 2510$ Å (the pulse is inverted); **3** –corresponding zero lines; **4** –calibration sinusoid with frequency 500 kHz.

To determine the dissociation rate, use was made of the ability of molecular oxygen, when the temperature is raised, to absorb light in the region 2200–2600 Å as a result of transitions from excited vibrational levels of the ground electronic state $X^3\Sigma_g^-$ to the state $B^3\Sigma_u^-$ (the Schumann–Runge system) ([3,4]). Analysis showed that the band spectrum of oxygen in this wavelength region is accompanied by a continuous background owing to broadening of the Schumann

Fig. 2. Temperature distribution behind the front of a shock wave moving in oxygen at a velocity of 2.8 km/sec

Figure 2: Fig. 2. Temperature distribution behind the front of a shock wave moving in oxygen at a velocity of 2.8 km/sec

Fig. 3

Figure 3: Fig. 3

–Runge continuum and transitions from the state $^3\Sigma_g^-$ to the unstable state $^3\Pi_u$ (^{5}); the lines entering into the bands are strongly reabsorbed.

A measurement carried out (by N. N. Sobolev and co-workers, and also by us) of the gas temperature at some distance from the leading front of the shock wave, from the emissive and absorptive power of the sodium D line, present in the gas as an impurity, showed that the gas temperature at these points of the flow approaches (for $T < 4000°$ K) the calculated value obtained from the Hugoniot adiabat under the assumption of equilibrium dissociation and the absence of losses to heat exchange and friction. This made it possible to establish the dependence of the magnitude of light absorption in oxygen on temperature and on the concentration of molecules (for the selected spectral regions). Under the conditions of our experiments it was found–

a relatively weak dependence of absorption on concentration and a more strongly expressed dependence on temperature were found. Thus, by the absorption of light it was possible to find the temperature distribution directly behind the front of the shock wave.

Measurement of the temperature in the indicated manner showed that at a shock-wave velocity of 2.7-3 km/sec and a pressure ahead of the shock wave $P_0 = 7.6$ mm Hg, the gas temperature directly behind the shock-wave front has a maximum and then falls, approaching the value calculated from the Hugoniot adiabat under the assumption of equilibrium dissociation (Fig. 2). The dimensions of this zone decrease with increasing shock-wave velocity and pressure. At high pressures, when appreciable dissociation is absent, the indicated temperature maximum behind the wave front is not observed.

Fig. 2. Temperature distribution behind the front of a shock wave moving in oxygen at a velocity of 2.8 km/sec

Fig. 3

The dimensions of the dissociation zone behind the shock wave in oxygen, obtained in a recently published work (^{6}) by measuring the density gradient with a Toepler apparatus, proved, within the experimental error, to be analogous to our results.

If it is assumed that the indicated zone under the given conditions corresponds to the course of a chemically nonequilibrium process, and if the thermal dissociation of oxygen is taken to proceed according to the scheme

$$O_2 + M \rightleftarrows O + O + M, \tag{I}$$

$$O_2 + O_2 \rightleftarrows O_3 + O, \tag{II}$$

$$O_3 + M \rightleftarrows O_2 + O + M, \tag{III}$$

then from the obtained dimensions of the nonequilibrium zone one can calculate the value of the rate constant of the oxygen dissociation reaction, since the decrease in temperature characterizes the growth of the concentration of atomic oxygen, and the change in concentration characterizes the rate of the dissociation reaction. A quantitative relation between the temperature gradient behind the shock wave and the rate of dissociation can be obtained by using the law of conservation of energy for a steady one-dimensional flow.

At a temperature $T = 3000\text{–}4000^\circ$K, the decomposition of ozone (reaction III) proceeds so rapidly that reactions (II) and (III) can be rewritten in the form

$$O_2 + O_2 \rightarrow O + (O + O_2). \tag{II'}$$

The rate constant of oxygen dissociation behind the shock wave obtained from the experiment (Fig. 3) is composed of the constant of direct decomposition of O_2 (reaction (I)) and the rate constant for the decomposition of O_2 with intermediate formation of ozone (reaction (II)).

The activation energy of reaction (II) is 99.2 kcal/mole ([7],[8]), which is somewhat less than the energy of direct dissociation of oxygen (118 kcal/mole). Therefore it would be natural to suppose that the dissociation of oxygen proceeds along the path of reaction (II′). If, however, one uses the value of the con-

rate constant of reaction (II), obtained in (8) for the temperature $T = 330—385^\circ$ K, $k_{II} = 6.7 \cdot 10^{12} \exp(-99200/RT)$ cm^3/mole • sec, is valid at high temperatures, then from the experimental results obtained by us it follows that the dissociation proceeds mainly by direct decomposition of O_2. The value of the pre-exponential factor P in the rate constant of reaction (I), written in the form of the Arrhenius relation $k_1(T) = PZ\exp(-D/RT)$ (where Z is the number of collisions of molecules per sec, D is the dissociation energy = 118 kcal/mole), in this case greatly exceeds unity and is equal (on average) to $P = 500$ at $T = 3000^\circ$ and $P = 150$ at $T = 3600^\circ$ K. In (7), for the rate constant of reaction (II) they assume $k_{II} = 3 \cdot 10^{12}\sqrt{T}\exp(-99210/RT)$ cm^3/mole • sec.

If, for estimating the rate of reaction (II), one takes this value, then the obtained value of the factor P decreases, but by no more than 10%.

Similar values of P, exceeding unity by several orders of magnitude, were also obtained in the case of the dissociation of certain other diatomic molecules, including bromine (9).

If the rate constant of the reaction $O_2 + O_2 \to O_3 + O$ at $T = 3000$—$4000°$ K in fact exceeds the above values of k_{II}, then it may turn out that this reaction will play a substantial role in the process of oxygen dissociation. Further experiments are necessary to clarify this question.

Moscow State University
named after M. V. Lomonosov

Received
5 III 1958

CITED LITERATURE

1. E. Resler, Sh.-C. Lin, A. Kantrowitz, J. Appl. Phys., **23**, No. 12, 1390 (1952).
2. I. I. Glass, G. N. Patterson, J. Aeronaut. Sci., **22**, No. 2, 73 (1955).
3. W. R. Garton, M. W. Feast, Nature, **165**, No. 4190, 281 (1950).
4. A. Hercog, K. Wieland, Helv. Phys. Acta, **23**, No. 4, 432 (1950).
5. P. G. Wilkinson, R. S. Mulliken, Astrophys. J., **125**, No. 2, 594 (1957).
6. H. S. Glick, W. H. Wurster, J. Chem. Phys., **27**, No. 5, 1224 (1957).
7. J. O. Hirschfelder, C. F. Curtiss, E. S. Campbell, J. Phys. Chem., **57**, No. 4, 403 (1953).
8. S. W. Benson, A. E. Axworthy Jr., J. Chem. Phys., **26**, No. 6, 1718 (1957).
9. H. B. Palmer, D. F. Hornig, J. Chem. Phys., **26**, No. 1, 98 (1957).

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