Physical Chemistry

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ON THE NONEQUILIBRIUM STATE BEHIND A SHOCK WAVE IN AIR

(Presented by Academician V. N. Kondrat’ ev on 17 III 1960)

At the high temperatures developing behind the front of a shock wave, air is a mixture of atoms and molecules of oxygen and nitrogen, as well as nitrogen oxides and other gases; study of the process by which equilibrium is established in such a mixture is a very difficult problem. In the present communication we set forth the results of a preliminary experimental investigation of the state of the gas behind a shock wave in air.

Fig. 1. Oscillogram of the distribution of absorption behind the front of a shock wave propagating in air with a velocity of 3.62 km/sec at an initial pressure of 4.4 mm. Straight line—zero level. Frequency of the calibration sinusoid—1 MHz

The experiments were carried out in a shock tube (ˆ1, ˆ2). In the high-pressure chamber of the shock tube, hydrogen was used at a pressure of 40-130 atm. In the low-pressure chamber there was purified air (purified by freezing out with liquid nitrogen) at a pressure of 4.4-7.6 mm Hg (0.0058-0.01 atm). The velocity of the shock wave was measured with ionization gauges with an accuracy of 1-2% and, depending on the initial pressure ratio in the chambers, varied from 2.4 km/sec to 3.7 km/sec.

Our earlier investigation (ˆ2) showed that, under the indicated conditions, the air behind the shock wave possesses appreciable absorptive capacity in the ultraviolet region of the spectrum ($\lambda < 3400$ Å). This property of heated air was used to study its state behind the shock wave. For this purpose the arrangement described in (ˆ2) was used; scattered light at $\lambda > 2170$ Å was practically not recorded by the photomultiplier. The resolving time of the entire recording channel was $\tau \sim 0.2\,\mu$ sec.

In the experiments, the distribution of the magnitude of the absorptive capacity behind the front of the shock wave in air was studied in a wavelength interval of 10 Å near $\lambda = 2200$ Å. It turned out that, at the above-mentioned pressure and shock-wave velocity, considerable absorption of light is observed immediately

Fig. 2

Figure 2: Fig. 2

behind the wave front; then, with increasing distance from the leading front, the magnitude of the absorptive capacity decreases and thereafter remains constant (Fig. 1). The region of constant absorption corresponds to the equilibrium state of the gas (according to (⁀3), in this region the measured temperature of the air agrees satisfactorily with the calculated temperature, computed on the assumption of complete chemical equilibrium).

To resolve the question of the reason for the appearance of the maximum of light absorption immediately behind the leading front of the shock wave, it is necessary to know,

how much and to what extent contributes to the observed absorption. Additional control experiments with N_2, O_2, and a mixture of 21% O_2 + 79% Ar ("air," in which nitrogen is replaced by argon) showed that the absorption observed in air at $\lambda = 2200$ Å is determined mainly by O_2 molecules; the absorption occurs as a result of transitions from the vibrationally excited levels of the ground state $X^3\Sigma_g^-$ to the state $B^3\Sigma_u^-$ (the Schumann–Runge bands of O_2). It was established that the absorptivity of air at $\lambda = 2200$ Å depends strongly on the concentration of O_2. Therefore, the decrease of the absorptivity in the flow behind the front of a shock wave may be associated with nonequilibrium dissociation of O_2 in air.

The dimensions of the zone in which the O_2 dissociation process occurs can be characterized by the distance $l_{0.5}$ from the leading front of the shock wave to the point at which the difference between the maximum value of the absorptivity and the constant absorption level decreases by a factor of two. The experimental dependence of this length $l_{0.5}$ on the mean temperature behind the front* for experiments in which the pressure behind the shock wave was 1 ± 0.18 atm is given in Fig. 2a. As can be seen from Fig. 2, the length of the nonequilibrium region decreases noticeably with increasing temperature, which can be explained by an increase in the dissociation rate of oxygen molecules.

Fig. 2. The obtained dependence of the characteristic length of the nonequilibrium zone in air (a) and in oxygen with a nitrogen impurity not exceeding 1% (b) on the mean temperature behind the shock-wave front at atmospheric pressure behind the wave. For oxygen, averaged data from this work (7) (solid line) and work (1) (dashed line) are shown. The dash-dotted line indicates the dimensions of the nitrogen vibrational relaxation zone according to data (8).

Let us consider a possible mechanism of reactions leading to a change in the concentration of O_2 in air, neglecting, in accordance with (4), the influence of recombination reactions, which begin to play a noticeable role only near equilibrium:

$$\begin{aligned} O_2 + O_2 &\rightarrow 2O + O_2 && \text{(I)} \\ O_2 + O &\rightarrow 3O + O && \text{(II)} \\ O_2 + N_2 &\rightarrow 2O + N_2 && \text{(III)} \\ O_2 + N &\rightarrow 2O + NO && \text{(IV)} \end{aligned}$$

To estimate the influence of nitrogen on the process of O_2 dissociation in air, it is of interest to compare the magnitude of the dissociation rate of O_2 in pure oxygen (reactions I, II) and in air. The presence of reactions III and IV leads to the fact that, at the same partial pressure of oxygen, dissociation of O_2 in air will proceed faster than the decomposition of O_2 in pure oxygen. The ratio r of the dissociation rates of O_2 in pure oxygen and in air will be different if the comparison is made at different partial pressures of oxygen. At the same temperature, it follows from scheme I—IV that

$$r = \left(\frac{P'}{P''}\right)^2 \frac{K_{\mathrm{I}}\xi'_{O_2}\xi'_{O_2} + K_{\mathrm{II}}\xi'_{O_2}\xi'_{O}}{K_{\mathrm{I}}\xi''_{O_2}\xi''_{O_2} + K_{\mathrm{II}}\xi''_{O_2}\xi''_{O} + K_{\mathrm{III}}\xi''_{O_2}\xi''_{N_2} + K_{\mathrm{IV}}\xi''_{O_2}\xi''_{N}}, \qquad (1)$$

where K are the rate constants of the corresponding reactions, ξ_M is the molar fraction of component M, and P is the total pressure; one prime refers to experiments in O_2, two primes to experiments in air. At the same total pressure ($P' = P''$), the presence of reactions III and IV in air (the last two terms in the denominator of relation (1)) may already fail to compensate for the fivefold increase in the partial pressure of O_2 ($\xi'_{O2} \sim 5\xi''_{O2}$)—the rate of dissociation of O_2 in air in this case may be less than the rate of dissociation of O_2 in pure oxygen. This is indeed observed experimentally at $P' = P'' = 1$ atm (Fig. 2): the nonequilibrium zone of O_2 dissociation in air at $\overline{T} \sim 3500 \div 4500$°K is longer than the dimensions of the zone in O_2.* For $P' = 0.5$ atm and $P'' = 1.2$ atm, it was found that at $\overline{T} = 4000$°K, $r \sim 1 \div 2$.

Comparison with (6) showed that the experimentally measured total rate of O_2 dissociation in air at atmospheric pressure, $-d\xi_{O2}/dt$, is approximately equal to $3 \cdot 10^8$ and $1 \cdot 10^9$ $\left(\mathrm{mol/cm^3}\right)^{-1} \cdot \mathrm{sec}^{-1}$ at $\overline{T} = 3500°$ and 4000°K, respectively. However, these quantities apparently give only an upper limit to the possible values, since the dimensions of the observed O_2 dissociation zone behind the wave front in air are somewhat underestimated because of the influence of the process of delayed excitation of N_2 vibrations, which occurs practically simultaneously with O_2 dissociation (Fig. 2). The higher temperature caused by the

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* The mean temperature behind the shock-wave front was determined as the arithmetic mean of the equilibrium value and the value obtained without taking into account the energy expenditure on dissociation. On the upper boundary of Fig. 2 is plotted the approximate calculated value of the magnitude of the temperature change in the process of O_2 dissociation in air for the corresponding value of the mean temperature.

delay in excitation of N_2 vibrations leads to a reduction in the time required for O_2 dissociation in air. This probably also affects the dependence of the characteristic length $l_{0.5}$ on $\overline{T}$.

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* An analogous result was obtained by Camac et al. (^{5}), who found that at the same total pressure ($P \sim 3.5$ atm), the establishment of equilibrium in O_2 also occurs more rapidly than in air.

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

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