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MEASUREMENT OF OXYGEN RECOMBINATION RATE CONSTANTS BY THE PIEZOELECTRIC METHOD

I. E. Zabelinskii and O. P. Shatalov

UDC 539.196+629.7.018.1

The piezoelectric method is used to measure pressure in a gas flow within a nozzle, measurement results are compared with calculation, and values of the oxygen atom recombination rate constant are obtained for the temperature range 1680-3250°K.

Calculation of parameters of hypersonic air coolant flows requires consideration of "reverse" processes - atomic recombination rates, molecular deactivation - and thus knowledge of the corresponding rate constants for such processes. However, at present such processes have been studied much more poorly than the corresponding forward ones. The goal of the present study was the measurement of oxygen recombination rates in a hypersonic cooling flow by recording pressure on the lateral walls of a planar wedge-shaped nozzle. This approach is based on the fact that in contrast to shock waves, where the density is the sensitive parameter of the kinetics, in a cooling hypersonic flow the pressure is the sensitive parameter.

Data available in the literature on the recombination rate constant k_r for the reaction $O + O + M \rightarrow O_2 + M$ are not numerous and vary amongst themselves by more than an order of magnitude. The analysis performed, for example, in review [1] concluded that it was impossible to recommend any value of k_r and proposed (for the range $T > 2000^\circ\text{K}$) that for the case $M = O_2$ recalculation from the values of the rate constant for oxygen dissociation should be used. (The recombination rate constant k_r is then determined from the kinetic equation $d[O_2]/dt = k_r[O]^2[M]$, where $[O_2]$, $[O]$, and $[M]$ are the concentrations of O_2 molecules, oxygen atoms O , and particles M , which latter play the role of third bodies in the recombination process.)

The experiments were performed in a shock tube with internal diameter of 49.3 cm. The gas (pure oxygen) was heated first in an incident, then a reflected shock wave to a state of partial dissociation, then escaped through a planar wedge-shaped nozzle, with an included angle of 15° , critical section height of 4 mm, and curved confusor section 8 mm in radius. Pressure sensors were installed on the face wall ahead of the nozzle entrance, allowing study of the characteristics of the gas heated by the reflected wave. Additional piezosensors were placed at distances of 46, 76, and 126 mm from the critical section [2].

The velocity of the incident shock wave was measured by film (thermal) sensors. The working material used was oxygen, heated in a reflected shock wave to a pressure of 8-33 atm and temperature of 3670-4470°K. This corresponds to an initial oxygen dissociation of 25-44%. Experimental conditions are presented in Table 1.

The nozzle and entire measurement complex were located near the tube face at a distance of 11.5 m from the high pressure chamber. The method for performing experiments in such a shock tube with nozzle is described in detail in [3]. The piezoelectric sensors used were precalibrated by pressure measurements in an incident shock wave with known equilibrium pa-

TABLE 1. Initial Experimental Conditions

P_1 , atm	V_s , m/sec	[O]	[O ₂]	P_s , atm	T_s , K
0,013	2380	0,25	0,75	8,0	3672
0,024	2500	0,28	0,72	16,9	3949
0,0245	2470	0,26	0,74	16,6	3919
0,026	2532	0,29	0,71	19,0	4002
0,025	2410	0,24	0,76	15,7	3852
0,029	2740	0,37	0,63	26,6	4261
0,031	2632	0,32	0,68	25,4	4153
0,031	2857	0,41	0,59	32,9	4416
0,028	2924	0,44	0,56	32,18	4470

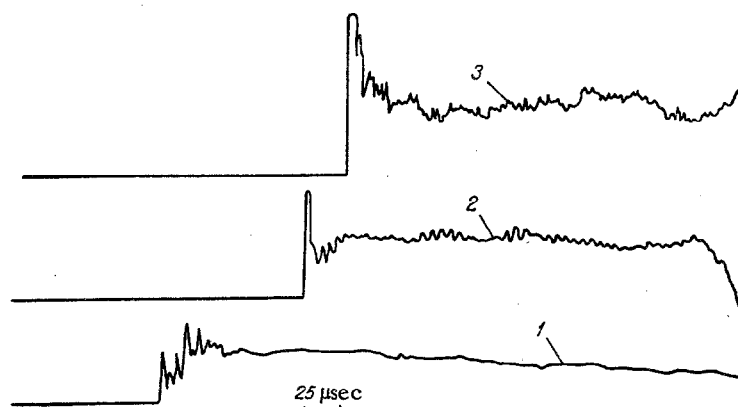


Fig. 1. Pressure oscillograms in nozzle and reflected shock wave, $P_s = 15.7$ atm, $T_s = 3582^\circ\text{K}$: 1) sensor in nozzle face; 2) sensor in nozzle, $x = 46$ mm; 3) sensor in nozzle, $x = 76$ mm.

rameters. The sensitivities of the sensors comprised 0.62, 0.54, and 0.42 V/atm. Calibration accuracy was $\pm 7\%$.

As the partially dissociated oxygen escaped from the nozzle the pressure sensors recorded the gas pressure, which depends on both the degree of expansion of the flow and the oxygen atom O recombination rate. Sensor signals were applied to the inputs of a multichannel transient process recorder, type DL-2800 with digital memory, then printed by a plotter and analyzed. An example of the recorded signals is shown in Fig. 1.

The experimentally measured pressure distribution of the recombining gas along the nozzle was compared with the results of a calculation carried out using various "test" values of the recombination rate constant.

The kinetic model and calculation program used to describe the recombining oxygen flow were described in [4], therefore we will only characterize them briefly here. The kinetic model considers processes of oscillatory relaxation of the oxygen, its recombination with formation of O₂ and O₃ molecules, exchange reactions in the presence of O atoms and oxygen and ozone atoms, and the interaction of oscillatory relaxation and dissociation processes. The problem of passage through a nozzle of specified profile of a supersonic flow of a chemically reacting and relaxing gas mixture was solved in the quasi-one-dimensional approximation. Initial conditions were defined from experiment, while in accordance with the recommendations of [1] in the first approximation the oxygen recombination rate constant was taken equal to a value obtained by recalculation of the dissociation rate constant. The calculation generates distributions of the recombining gas parameters along the nozzle, in particular, the pressure, and the "test" recombination rate constant was varied to achieve agreement with the experimental values obtained in each of the three nozzle sections. Values of k_r obtained for the reaction $O + O + O_2 \rightarrow O_2 + O_2$ in the temperature range $T = 1680\text{--}3250^\circ\text{K}$ are presented in Fig. 2.

Before turning to evaluation of the results obtained, it is necessary to note the following. First, in the escape regimes studied the sensitivity of gas pressure within the nozzle to change in the recombination rate constant proved to be quite low — pressure changed less than 20% for an increase or decrease in k_r by a factor of five times. Therefore, determination of

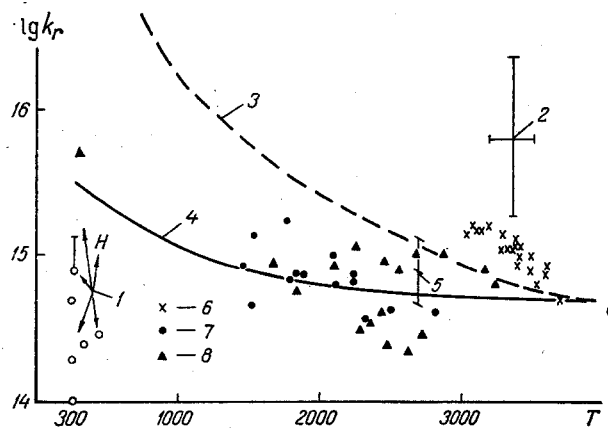


Fig. 2. Oxygen recombination rate constants for reaction $O + O + O_2 \rightarrow O_2 + O_2$, $\text{cm}^6/(\text{mole}^2 \cdot \text{sec})$: 1) data at $T \sim 300^\circ\text{K}$ [1]; 2) data of [6], $M = 0$; 3) extrapolation to low temperature range of k_r values obtained with oxygen dissociation rate constant for $T > 4000^\circ\text{K}$; 4) approximation by Eq. (1); 5) data of [8]; 6) data of [7]; 7) data of [5]; 8) results of present study (except leftmost triangle, which is from [1]).

constants to an accuracy better than a factor of two times proved impossible, leading to significant scattering of the experimental results. Second, it is obvious that aside from O_2 molecules the role of third bodies is also played by O atoms, upon which oxygen recombination occurs. (The molar fraction of ozone molecules in the experiments comprised less than 10^{-5} , therefore their effect on k_r can be neglected.) The recombination rate constant for $O + O + O \rightarrow O_2 + O$ was not studied separately, but from what is known of reverse reaction rate constants, it was taken equal to three times the value of the constant $k_r(M = O_2)$. Data exist [1] indicating that efficiency of O atoms in the recombination process may be comparable to that of O_2 molecules or even lower, so that the assumption used $k_r(M = O) = 3k_r(M = O_2)$ introduces additional error into the results. However, calculations show that the error does not exceed the scattering of the points shown in Fig. 2, since the O atom concentration is less than 50% even at the nozzle input and falls off constantly along the nozzle. However, if the real efficiency of atoms is higher than that used in the calculations the results obtained herein are systematically elevated.

Third and finally, all the flow regimes studied herein are "kinetic," i.e., recombination does not "freeze" along the nozzle length even at the farthest removed sensor, located 126 mm from the critical section. This is explained by the high value of the nozzle critical section, the low aperture angle, and the initial gas pressures, quite high for the profile and k_r values obtained. The presence of a recombination regime along the entire nozzle permits referring the k_r values obtained to temperatures corresponding to the nozzle section at which the pressure measurement was performed.

Analysis of the k_r values obtained with consideration of the results of [5], performed in approximately the same temperature interval (by density measurements), and numerous, albeit quite scattered, measurements at room temperature indicates that in the temperature range $T = 298\text{--}4000^\circ\text{K}$ values of the recombination rate constant $k_r(M = O_2)$ are lower than values obtained by recalculation of the high temperature rate constant of the reverse process (shown in the figure by the dashed curve). There is a slight tendency to decrease in k_r value with growth in temperature. In the temperature range $298\text{--}4000^\circ\text{K}$ the measured constant is described well by the following expression, which passes through the available experimental points in the interval $T = 1680\text{--}3250^\circ\text{K}$ and considers the data of [1] obtained at lower temperature:

$$k_r = 8.91 \cdot 10^{16} T^{-0.63}, \quad (1)$$

with $M = O_2$, and accuracy within a factor of two times.

It is obvious that it is necessary to both increase the accuracy of the measured rate constant and to obtain data in lower temperature ranges, from 300 to 1500°K , where the rate constant has not been studied sufficiently.

NOTATION

k_r , recombination rate constant for oxygen atoms; $K_r(M)$, oxygen recombination rate constant with particle M playing role of catalyst; $[O]$, $[O]_2$, $[M]$, concentrations of O, O_2 , and M particles; P_1 , initial gas pressure in shock tube; P_5 , pressure in reflected shock wave; V_s , shock wave velocity; T_5 , gas temperature in reflected shock wave.

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EXPERIMENTAL EVALUATION OF THE EFFICIENCY OF TEMPERATURE DIAGNOSIS OF FRICTION

I. N. Cherskii, O. B. Bogatin,
N. P. Starostin, V. V. Donchenko,
and G. I. Balanov

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Results are reported from an experimental evaluation of the efficiency of determining the moment of friction in a cylindrical coupling from measurements of temperature inside the bushing.

In [1], we attempted to solve the problem of identifying heat release in a cylindrical coupling from measurements of the temperature of the rubbing bodies. Determination of this quantity allowed us to determine the friction work of the sliding contact, since it is known that most of this work is converted into heat [2, 3].

To evaluate the efficiency of the method employed in this case, we experimentally checked the determination of the friction moment as a function of time from temperature measurements. The results of this investigation are reported here.

In [1], we used an idealized planar thermal model. To construct the thermal model of the test element, it is necessary to consider heat removal along the axis of the shaft (Fig. 1). Here, the following simplifications are made: the temperatures in the cross sections of the shaft and along the bushing are uniform; heat exchange with the ends of the bushing is not considered. Also, in formulating the boundary conditions, we used the measurement of shaft temperature far from the friction zone. Then the heat conduction equation for the shaft is written in the form:

$$c_2 \rho_2 \frac{\partial u}{\partial t} = \lambda_2 \frac{\partial^2 u}{\partial z^2} - \frac{P}{S} \alpha_s (u - T_0) + \left[Q(t) + 2r_2 \lambda_{1d} \int_0^{\varphi_2} \frac{\partial T(r_2, \varphi, t)}{\partial r} d\varphi \right] \frac{\theta(z)}{Sd}, \quad (1)$$

Institute of Physicotechnical Problems of the North, Yakutsk Branch, Siberian Department of the Academy of Sciences of the USSR, Yakutsk. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 53, No. 3, pp. 442-446, September, 1987. Original article submitted June 30, 1986.