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EXPERIMENTAL INVESTIGATION OF NONEQUILIBRIUM PROCESSES BEHIND A SHOCK WAVE IN AIR AND NITROGEN BY THE SHADOW METHOD

(Presented by Academician I. V. Obreimov, 29 X 1968)

Of great interest for modern aerophysics is the investigation of the complex of phenomena occurring in strong compression shocks in air and its components. As a result of the transformation, in a compression shock, of a considerable part of the energy of the translational motion of molecules into its other forms, molecular rotation is successively intensified, vibrations arise, as do dissociation, electronic excitation, and ionization.

Different times are required for the excitation of each of these forms of internal energy, which are substantial at certain sufficiently high temperatures and pressures behind the shock wave. In the range of temperatures and pressures under study, the translational and rotational degrees of freedom, as well as the vibrational degrees of freedom, come to equilibrium considerably faster than noticeable dissociation and ionization of the components of air occur ([1]).

According to existing theoretical and experimental data, immediately behind the wave front there is a considerable increase in pressure and temperature.

As theoretical calculations and experimental studies have shown ([1,2,8,10]) and others, the time for vibrational excitation in nitrogen and oxygen under the conditions considered is also much less than the time required for noticeable dissociation. Thus, the temperature in the shock wave before the onset of dissociation reaches, depending on the shock-wave velocity, $\sim 5000 \div 10\,000^{\circ}$K, and then falls to an equilibrium temperature of $\sim 3000 \div 7000^{\circ}$K; by the end of the process, equilibrium dissociation is also attained.

The phenomena behind a shock wave in air are more complex because of the presence of additional chemical reactions of its components.

Fig. 1

Figure 1: Fig. 1

The aim of the present work was to investigate nonequilibrium processes behind a shock wave in nitrogen and air: to determine the dimensions of the nonequilibrium zones behind the shock wave, to estimate the rate constant of recombination in nitrogen, and to measure the refractive coefficient of atomic nitrogen needed to obtain density data in the study of partially dissociated gases.

The high temperature and the proper degree of dissociation in our experiments were achieved in a shock tube ([15]). The high and low pressures in its sections were chosen in such a way that changes in the refractive index due to the dissociation process of the gas under investigation could be measured. The upper limit was determined by the sensitivity of the shadow apparatus, since a temperature of the order of 8000°K could be obtained only with a low flow density, at which changes in the refractive index caused by the dissociation process could not be measured; the lower limit was determined by the presence of noticeable dissociation.

To investigate nonequilibrium processes behind a shock wave in air and nitrogen, a shadow photoelectric method was used ([3]). A typical

an oscillogram of the time sweep of the process of shock-wave passage is shown in Fig. 1. Here I is the shock-wave front, t_1, t_2 are the regions of uniform parameters (the working section) and of nonequilibrium processes, and t_3 is the contact region.

The amplitude of the experimental curve at each point is proportional to the gradient of the refractive index of the gas under study at the corresponding point of the flow behind the shock wave. Applying the procedure for interpreting the quantitative shadow photoelectric method ([3]), one can obtain the refractive-index gradient $\dfrac{\partial n}{\partial x}(t)$ at each point of the process. On the rectilinear portion of the characteristic curve, the signal amplitude A is proportional to the gradient of the refractive index of the gas under study

Fig. 1. a—oscillogram with a long sweep; b—oscillogram with a short sweep

$$\partial n/\partial x = A \operatorname{ctg} \beta / FL,$$

where β is the angle of inclination of the characteristic curve, F is the focal length of the shadow instrument, and L is the optical path length of the light in the inhomogeneity. The area under the curve $\partial n/\partial x = f(x)$ in the interval t_2 determines the increase in the refractive index of the gas under study. The subsequent growth of the refractive index is connected with the appearance of the contact region.

In the region of nonequilibrium processes behind the shock wave there exists a mixture of atomic and molecular nitrogen. Since no strong intermolecular interaction arises when they are mixed ([4]), then

$$n - 1 = k_{\mathrm{N}} N_{\mathrm{N}} + k_{\mathrm{N2}} N_{\mathrm{N2}}, \tag{1}$$

where n is the refractive index of the mixture of two gases; N_{N} and N_{N2} are, respectively, the numbers of particles of atomic and molecular nitrogen per unit volume ([4]), $k_{\mathrm{N}} = 3R_{\mathrm{N}}/2N_a$, $k_{\mathrm{N2}} = 3R_{\mathrm{N2}}/2N_a$. Here R_{N} and R_{N2} are, respectively, the refractions of N and N_2; N_a is the number of particles in 1 g-mole.

Changes in the refractive index introduced by ionized atoms may be neglected, since the degree of ionization in the temperature range considered is small. k_{N} and k_{N2} are almost independent of temperature ([5]). Deviations are appreciable only upon excitation of electronic energy levels. k_{N2}, which determines the refraction of nitrogen, is well known and is equal to $1.13 \cdot 10^{-23}$ cm^3; k_{N} can be determined from equation (1), if at some point of the mixture the refractive index and the number of particles of each gas are known.

N_{N} and N_{N2} are related to the degree of dissociation α by the relation

$$\alpha = \frac{N_{\mathrm{N}}/2}{N_{\mathrm{N}}/2 + N_{\mathrm{N2}}}. \tag{2}$$

The gas parameters in the flow behind the shock wave can be calculated behind the shock front ($\alpha = 0$) and in the region of thermodynamic equilibrium ($\alpha = \alpha_{\mathrm{eq}}$); the temperature and pressure are calculated on the basis of the measured velocities of the shock-wave front and the initial conditions ([1,14]).

Use of one of the boundary conditions makes it possible to find the refractive index at the initial point $n = n_0$. The refractive index at any other point of the flow x is determined by numerical integration

of the experimental curve $\partial n/\partial x = f(x)$

$$n(x) = n_0 + \int_{x_0}^{x} \frac{\partial n}{\partial x}\, dx. \tag{3}$$

The directly obtained curve represents the dependence $\dfrac{\partial n}{\partial x}(t)$, where t is time. The transition from $\dfrac{\partial n}{\partial x}(t)$ to $\dfrac{\partial n}{\partial x}(x)$ can be carried out if the velocity of motion of the gas particles V at various points of the flow is known. From (1) and (2) we obtain

$$k_N = [n - 1 - k_{\mathrm{N2}}(1-\alpha)n_m]/2\alpha n_m, \tag{4}$$

where n is the refractive index at a certain point of the flow; n_m is the number of particles per unit volume at the same point, with

$$n_m = N_N/2 + N_{\mathrm{N2}}.$$

Using relation (3), we obtain

$$k_N = \frac{1}{2\alpha_{\mathrm{eq}}}\left\{\int_{x_0}^{x_{\mathrm{eq}}} \frac{\partial n}{\partial x}\,dx/n_{m\mathrm{eq}} - k_{\mathrm{N2}}\left(1 - \alpha_{\mathrm{eq}} - \frac{T_{\mathrm{eq}}}{T_{\mathrm{v.f}}}\right)\right\}. \tag{5}$$

Here x_{eq} is the coordinate of the point in the flow corresponding to the region of equilibrium parameters; α_{eq}, $n_{m\mathrm{eq}}$, T_{eq} are, respectively, the degree of dissociation, the total number of particles per unit volume, and the temperature at this point; $T_{\mathrm{v.f}}$ is the temperature of the gas behind the shock wave when the vibrational degrees of freedom are fully excited.

Table 1

P_n, mm	$T_{\mathrm{v.f}}$ (vibr.), °K	k_r, cm^6/mole^2 · sec
1	7130	$1.08 \cdot 10^{18}$
1	6000	$3.96 \cdot 10^{16}$
1	5940	$1.33 \cdot 10^{15}$
3	5350	$1.28 \cdot 10^{13}$
5	4730	$3.78 \cdot 10^{12}$

Processing of the experiments showed that the course of the experimental curve in the region t_2 can be represented by the exponential $\partial n/\partial x = e^{-B_0 x + A_0}$. Here A_0 and B_0 are constants for the given experiment, determined from the graph $\ln(\partial n/\partial x) = f(x)$.

The mean value $R_N = 10.41 \cdot 10^{-24}$ cm^3, which agrees with theoretical ([12]) and experimental ([13]) data.

The relation between the change in the number of particles and the reaction-rate constant is written in the form

$$dN_N/dt = k_{dN_{\mathrm{N}}2} n_m - k_{rNN}^2 n_m. \tag{6}$$

Here k_r and k_d are, respectively, the rate coefficients of recombination and dissociation, with $k_d/k_r = k_c$, where k_c is the thermodynamic-equilibrium constant.

From (6), using the preceding expressions, we obtain

$$\frac{dN_N}{dt} = \frac{2d(\alpha n_m)}{dT}\frac{dT}{dn}\frac{dn}{dx}\frac{dx}{dt}; \tag{7}$$

$$dn/dT = d[2\alpha n_m k_N - k_{\mathrm{N2}}(1-\alpha)n_m]/dT. \tag{8}$$

Substituting (8) into (7) and equating to (6), we obtain

$$k_r = \frac{2(dx/dt)(dn/dx)}{n_m^2\,[2k_N - k_{\mathrm{N2}}(1 - dn_m/d(\alpha \cdot n_m))]\,[k_c(1-\alpha) - 4n_m\alpha^2]}. \tag{9}$$

The quantity $dn_m/d(\alpha n_m)$ can be neglected at the initial moment because of its smallness.

The results of the experiments are presented in Table 1. The values of k_r are referred to the equilibrium vibrational temperature. Analysis of the data shows that the obtained values of k_r are closer to data (6) than to (16).

The experimental data obtained made it possible to find the times of vibrational and dissociation relaxation in nitrogen and air.

The logarithms of the relaxation times for nitrogen and air, reduced to atmospheric pressure, as functions of the equilibrium temperature, are shown in Fig. 2. It should be noted that in some experiments two relaxation zones were obtained (Fig. 1b). In this case the relaxation time in the first zone was taken as the vibrational relaxation time, and in the second zone as the dissociation relaxation time. Such results were obtained with nitrogen at equilibrium temperatures $T_p \approx 4000 \div 5000^{\circ}\mathrm{K}$ (Fig. 2).

Fig. 2. Data on the relaxation time for air and nitrogen (dependence of the relaxation time τ, reduced to atmospheric pressure, on the equilibrium temperature).
1 —experimental relaxation time for O_2 vibrations $(1, 6, 10)$;
2 —relaxation time for O_2 dissociation (1);
3 —relaxation time for N_2 vibrations $(1, 8, 10)$;
4 —relaxation time for N_2 dissociation (8);
5 —experimental relaxation time for NO formation (9).
Data of the present work: a —relaxation time for nitrogen; b —relaxation time for air; c —relaxation time for nitrogen with an admixture of air.

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