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Abstract

Full Text

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ON THE QUESTION OF THE RATE OF PHYSICOCHEMICAL TRANSFORMATIONS OF CO₂ MOLECULES BEHIND A SHOCK WAVE AT TEMPERATURES OF 2000-4000 °K

(Presented by Academician V. A. Kirillin on 15 VIII 1963)

From the values of the gas-dynamic parameters of the flow behind a shock wave one can judge the rate of physicochemical transformations of gas molecules. In particular, the nonequilibrium of chemical reactions substantially affects the state behind a shock wave in carbon dioxide. The depth of dissociation and the degree of excitation of CO₂ molecules at temperatures of 2500-4500 °K are sufficiently large, while the relaxation times of these processes reach several hundred microseconds at such temperatures. According to preliminary data, the delay times for dissociation of CO₂ molecules in the temperature range from 3000 to 6000 °K are 600-100 μsec (at a pressure of 1 atm.) ⁽¹⁾. There are data on substantially different relaxation times for excitation of vibrations of CO₂ molecules. The linear triatomic CO₂ molecule has three types of vibrations: deformation vibrations with frequency $\nu_2 = 672 \text{ cm}^{-1}$, symmetric valence vibrations $\nu_1 = 1341 \text{ cm}^{-1}$, and asymmetric valence vibrations, whose frequency is $\nu_3 = 2347 \text{ cm}^{-1}$.

Deformation vibrations in the temperature range 1500-3000 °K are excited in times $\tau_1 = 1-3 \text{ μsec}$ ⁽²⁻⁴⁾. On the question of the excitation times of symmetric valence vibrations in the indicated range of T , there is as yet no single opinion. Some authors ⁽³⁾ consider that, at least up to temperatures of 2500 °K, valence vibrations are excited in times 1.5-2 orders of magnitude greater than τ_1 ; others ⁽⁴⁾ suppose that excitation of deformation and symmetric valence vibrations should occur practically simultaneously in the indicated temperature range. Longer relaxation times should be expected for asymmetric valence vibrations.

The processes of vibrational excitation and dissociation of molecules, and the relaxation of these processes, affect the parameters of the gas flow behind the discontinuity.

Fig. 1

Figure 1: Fig. 1

The quantities most sensitive to the depth of attainment of equilibrium are temperature, density, and the speed of sound. The pressure depends only weakly on the degree of attainment of equilibrium. The velocity of the gas flow in the sample in the equilibrium state differs from the flow velocity in the completely frozen state by almost a factor of two, if the velocity is compared in the coordinate system associated with the wave; in the laboratory coordinate system associated with the walls of the shock tube, this difference is 10-15% (for wave Mach numbers $M_0 = 6 \div 11$).

On the basis of the graphs in Fig. 1, a comparison can be made of the temperature values behind a shock wave propagating in CO_2 , under the assumption of different degrees of excitation of the molecules.

Depending on the state of the gas molecules, the propagation velocity of an acoustic signal in gas heated by a shock wave of a given velocity may differ by a factor of 1.5.

In connection with this circumstance, determining the propagation velocity of a small disturbance can provide information on the degree of excitation of gas molecules in the flow behind a shock wave.

Our experimental investigations consisted in determining the parameters of the flow behind a shock wave from the flow around an obstacle placed in a shock tube.

The registration method used consisted in visualizing the process of flow around a half-wedge by the Toepler method, using high-speed spark photography (frequency $\sim 60\,000\text{ s}^{-1}$) (5). The investigations were carried out in a tube whose total length was 5.5 m. The chamber had a square cross section of $40 \times 40\text{ mm}^2$; the length of the low-pressure chamber from the diaphragm to the viewing section was 2.7 m, and the length of the viewing section was 20 cm. The synchronization scheme for the series of illuminating flashes with the process under study was analogous to that described in (5).

Fig. 1. Dependence of the temperature behind the shock wave on the shock-wave velocity in CO_2 .

a –completely equilibrium state of the gas in the flow; *b* –state with frozen dissociation and completely excited vibrations; *v* –state with frozen dissociation and frozen asymmetric valence vibrations; *g* –state with frozen dissociation and completely frozen vibrations of the molecules.

The angle of inclination of the Mach line, the angle of inclination of the oblique shock, and the Mach number of the propagating shock wave were recorded. Experimental results were obtained in the range of Mach numbers $M_0 = 6 \div 11$, at an initial pressure $P_0 = 10\text{ mm Hg}$.

Fig. 2

Figure 2: Fig. 2

From the angle of inclination of the Mach line we determined the Mach number M_1 of the incident flow.

A sequential calculation was carried out for the dependence of M_1 on M_0 for a number of equilibrium states of the gas in the flow behind the shock wave, taking into account different degrees of excitation of the molecules and assumptions concerning the speed of sound propagation in the flow.

Under the conditions of our experiment, on the basis of the results of works (6-11), it should be expected that the angle of inclination of the Mach line will be determined by the high-frequency—“frozen”—speed of sound (12, 13). The calculated dependences are presented in the graph of Fig. 2. Curve 1 was calculated under the assumption of equilibrium dissociation and equilibrium excitation of the vibrations of CO_2 molecules in the flow behind the shock wave, and of the displacement of equilibrium in the sound wave in accordance with the change in temperature and pressure in it.

Curve 5 gives the dependence of M_1 on M_0 under the assumption of frozen dissociation and “frozen” vibrations of the gas molecules in the flow, and of the absence of additional excitation of the molecules in the sound wave—i.e., of a “frozen” speed of sound.

In calculating the dependence shown by curves 2 and 3, it was assumed that the flow velocity and temperature correspond to a state with frozen dissociation and excited internal degrees of freedom of the molecules. In accordance with the assumption made regarding the value of the speed of sound in the medium, two curves were obtained. Curve 2 corresponds to the equilibrium speed of sound, curve 3 to the frozen speed of sound.

Fig. 2. Dependence of the Mach number of the flow M_1 on the Mach number of the propagating shock wave M_0 in CO_2 . Curves are calculated; points are experimental values.

If, for CO_2 molecules, the asymmetric valence vibrations are also considered unexcited, and it is assumed that a small perturbation propagates with the “frozen” speed of sound calculated with the heat-capacity ratio $\gamma = 1.4$, then the dependence of M_1 on M_0 will be represented by curve 4.

The experimentally obtained values are distributed around this curve.

On the basis of the calculations described and of the analysis undertaken of the experimental data, we have drawn the following conclusions about the state of CO_2 in the flow behind the shock wave. In the range of Mach numbers $M_0 = 6-11$, at an initial gas pressure in the shock tube of $p_0 = 10$ mm Hg, behind the shock wave at a distance of 5-15 cm from the discontinuity (over times on the

order of 100-250 msec), dissociation of CO_2 molecules does not occur. The vibrations of the CO_2 molecules are not fully excited by the time of observation. The asymmetric valence vibrations do not have time to become excited.

The Mach lines in the flows in the shock tube under the regimes studied have a direction determined by the frozen speed of sound, calculated with $\gamma = 1.4$.

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