EXPERIMENTAL INVESTIGATION OF THE EMISSION IN THE UNSTEADY FLOW REGION BEHIND STRONG SHOCK FRONTS IN MIXTURES OF CO AND CO₂ WITH NITROGEN AND ARGON

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Mixtures of CO (or CO₂) gases and N₂ behind strong shock fronts at temperatures 4000-10 000 K have been investigated with a view to elucidating the mechanism of the physicochemical processes in the unsteady region of the gas flow behind a shock front leading to the behavior of strongly radiating CN and C₂ molecules and C atoms and also determining the quantitative characteristics of the chemical reactions. A shock tube was used in the investigations, which made it possible to obtain the intensity distribution of the radiation of several components — CN, C₂, and C — behind shock fronts.

1. Discussion and Formulation of the Problem

One of the main problems in hypersonic gas dynamics concerns the parameters of the high-temperature gas stream behind strong shock fronts. Knowledge of these parameters, which depend strongly on the physicochemical processes that take place in the shock waves, permits correct solution of many applied problems. Many studies, both theoretical and experimental, have been devoted to the physicochemical processes in complex gas mixtures at high temperatures, for example, in air [1]. The physicochemical processes in CO₂–N₂ gas mixtures have been less well studied.

In the earlier shock tube experiments, made mainly in the sixties [2-5], only one molecular component was, as a rule, observed. Absence of data on the mechanism and rates of excitation of the molecular electron states and the presence in the high-temperature gas mixture of a large number of components and chemical reactions with unknown rates meant that it was not possible to identify the main processes governing the quantitative behavior and evolution of the radiation intensity of molecules and atoms behind a shock front. More recently, there have been experimental and theoretical investigations into the relaxation of the internal degrees of freedom of molecules, the dissociation and recombination of many molecules, and also a number of exchange reactions. This has made it possible to carry out a more complete and systematic investigation of the kinetics of the physicochemical processes in a high-temperature CO (CO₂)–N₂–Ar gas mixture.

The radiation in the spectra of the molecules CN and C₂ and C atoms observed in a shock tube gives information on the population of the corresponding excited electron states, and it is therefore important to know the excitation mechanisms and times for the electron states. In accordance with the mechanism of [6], equilibrium excitation of the electron states occurs during a time comparable with the time of the rotational–vibrational relaxation of the molecules. Since the processes which establish equilibrium with respect to the internal degrees of freedom proceed much faster than the chemical relaxation, it can be assumed that at each instant the rotational, vibrational, and electron degrees of freedom behind the shock front are in equilibrium with the translational degrees of freedom and that a Boltzmann distribution with temperature corresponding to the instantaneous translational temperature exists for all the energy states of the CN molecules. We assume that this conclusion is also valid for the other molecules and atoms formed in the shock wave, so that at each time t in the unsteady region of the flow (which is characterized by the absence of thermodynamic equilibrium and non-stationary radiation) the radiation intensity \( I_t \) satisfies

\[
I_t \sim [A] \exp\left(-\frac{E^*}{kT_t}\right)
\]
where $[A]_t$ is the concentration of component $A$, $E^*$ is the energy of the radiating electron state, $T_t$ is the instantaneous translational temperature, and $k$ is Boltzmann's constant.

The relation (1.1) establishes the dependence of the intensity $I$ on only the concentration of the component and the instantaneous temperature, making it possible to explain the distribution $I = f(t)$ in the unsteady flow region behind the shock front only by means of the kinetics of the chemical reactions involved in the formation of the corresponding component. Therefore, the oscillograms of the radiation of the molecules CN and $C_2$ and the atom C obtained in the experiment behind the shock front were the initial data for establishing the mechanism of the chemical reactions in the $CO_2-N_2$ gas mixture at high temperatures.

We assumed that in the shock front all the internal degrees of freedom of the components of the gas mixture have an equilibrium excitation. In the temperature range 4000-10 000 K, ionization processes can be ignored, and electrons and ions can be eliminated from the number of considered components of the gas mixture. Also ignored were the triatomic molecules NO$_2$, N$_2$O, C$_3$, O$_3$, N$_3$ formed in the shock wave in the chemical reactions, because they dissociate rapidly at $T \sim 4000$ K. Under these assumptions, the initial CO (or CO$_2$)-N$_2$-Ar gas mixture behind the shock front consists of ten chemically active components, N, C, O, N$_2$, C$_2$, O$_2$, NO, CO, CN, CO$_2$, and one inner component: Ar.

The investigation consisted of three stages: the experiment to measure the radiation intensity of the molecules CN and $C_2$ and the C atoms behind the shock front in the shock tube; numerical calculation of the flow parameters of the chemically reacting gas behind the shock fronts with simultaneous calculation of the radiation intensity of the CN, $C_2$, and C; comparison of the calculated and experimental distributions of the radiation intensity of the components behind the shock front and subsequent choice of the most reasonable kinetic model of the chemical reactions in the considered gas mixture.

2. Experimental Method

The experiments were made with a stainless steel shock tube of internal diameter 50 mm, low-pressure chamber 5-m long, and high-pressure chamber 1.5-m long. Hydrogen was used as the propelling gas in the high-pressure chamber. Before the experiment, the low-pressure chamber was filled with CO-N$_2$-Ar or CO$_2$-N$_2$-Ar gas mixtures at pressure 5-20 torr. The initial composition of the mixtures varied in a wide range. The shock wave velocities were measured by means of piezosensors at the observation sections of the shock tube and digital frequency meters. The errors in the measurements of the velocities by this method were not more than 1%. The measured velocities were in the range 2.5-3.5 km/sec.

The radiation from the shock tube was detected by appropriate optical schemes. The radiation from the shock tube, which passed through a spectral instrument or a light filter and corresponded to a definite section in the band spectra of the CN and C$_2$ molecules or a line of the C atom, was detected by means of photomultipliers and a five-beam oscillograph. The CN radiation was observed in the band (0, 1) of the violet system of bands (transition $B^2\Sigma^+ \rightarrow X^2\Sigma^+$). The instrumental function was trapeziform with the parameters $\lambda_0 = 421.1$ nm and $\Delta \lambda = 1.96$ nm (the lower base of the trapezium). The radiation of the C$_2$ molecules was detected in the (0, 0) band of the Swan system (transition $d_3^{3\Pi_g} \rightarrow a_3^{3\Pi_u}$, visible part of the spectrum). The instrumental function had the parameters $\lambda_0 = 516.5$ nm and $\Delta \lambda = 3.5$ nm. Information about the change in the concentration of the carbon atoms behind the shock front was obtained by detecting radiation in the resonance line $\lambda = 247.856$ nm of the carbon atom, which corresponds to transition from the highly excited electron term $2p^23s^1p$ (61982.2 cm$^{-1}$) to one of the lower excited terms $2p^23p^1S$ (21648.4 cm$^{-1}$). The radiation of this line was separated by means of a monochromator and photomultiplier sensitive to the ultraviolet part of the spectrum. The parameters of the instrumental function were $\lambda_0 = 247.8$ nm and $\Delta \lambda = 0.6$ nm.

Special experiments were made to verify the condition for an optically thin layer for the radiation of the cyanogen and C atom. This showed that under the conditions of the experiments there was no self-absorption of the CN and C radiation in a wide range of concentrations of these components, i.e., the radiation intensity was proportional to the concentration of the i-th component. We did not test for self-absorption of the C$_2$.