

Complex study of nonequilibrium phenomena in shock wave front in the various noble gases containing small admixture of $\text{Fe}(\text{CO})_5$

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1 Introduction

The purpose of the study is a linking analysis of nonequilibrium radiation picks observed in shock-heated mixtures of noble gases with a small admixture of $\text{Fe}(\text{CO})_5$. Two different mechanisms for this phenomenon are discussed – high energy collisions in the zone of translation relaxation and recombinative overexcitation of iron clusters formed as a result of the fast dissociation of $\text{Fe}(\text{CO})_5$ behind the shock wave. The first mechanism is based on results of works [1-5]. The second mechanism is based on results of works [6-7]. Analysis of experimental data based on the results of the Monte Carlo non-stationary method of statistical simulation (MCNMSS) (another name DSMC) and kinetic calculations could bring the bright insight in these complex phenomena.

2 Results of MCNMSS

The Monte Carlo non-stationary method of statistical simulation with constant weighting factors [1] was used to obtain velocity distributions of molecules in the shock wave front and make analysis of possible influence of high energy collisions on appearance of radiation picks.

A mixture of He and $\text{Fe}(\text{CO})_5$ was considered. Molecules were considered as hard spheres without internal structure. Ratio of molecular masses was set as 1:49, ratio molecular diameters was set as 1:3 respectively. Average number of the particle per cell ahead of the front was equal to 12000.

Parallel calculations were carried out by means of a multi-processor computer. And 8 processors of MVS100K of JSCC RAS were used. Schema of fine grain parallelism [8] was employed,

Figures 1-2 show results for the case of shock wave Max number (M) equal to 3.5 and of mixture containing 0.01% of $\text{Fe}(\text{CO})_5$ (n_2).

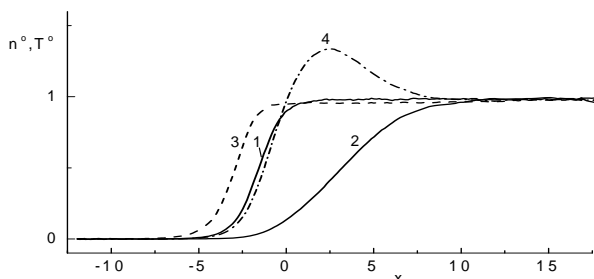


Figure 1.

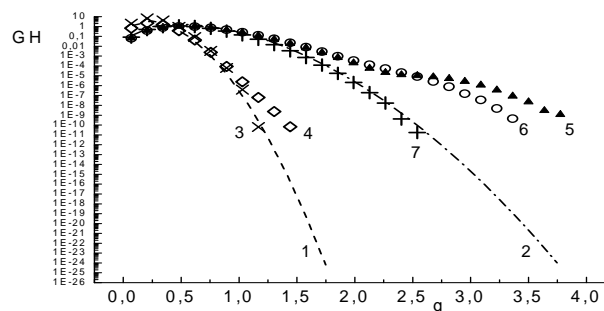


Figure 2.

The profiles of relative concentrations $n_i^o = (n_i - n_{ia}) / (n_{ib} - n_{ia})$ and kinetic temperatures $T_i^o = (T_i - T_a) / (T_b - T_a)$ of components are presented in Figure 1. Indices a and b refer to the variables ahead of and behind the shock wave. The distance x along the stream was normalized to the λ (λ is the mean free path of molecules ahead of the front). Curves 1 and 2 are profiles of relative concentrations of He and $\text{Fe}(\text{CO})_5$ respectively. Curves 3 and 4 are profiles of relative temperatures of He and $\text{Fe}(\text{CO})_5$. Figure 2 shows distributions GH of relative velocities g for pairs containing molecules of $\text{Fe}(\text{CO})_5$. Velocities are normalized to the sound velocity in the gas mixture ahead of the wave, while GH is normalized so that its integral is equal to 1. Curves 1 and 2 are equilibrium GH ahead of and behind the wave, 3 and 7 - the GH obtained at the left and right sides of the modeling region, 4-6 - GH in the front: (4) $x = -4.575$; (5) $x = 2.175$; (6) $x = -1.575$. As one can see GH exceeds substantially its equilibrium values behind the wave. Observed maximal overshoot (MO) is about 10^{15} (see distribution 5). Obtained distributions GL of g for pairs containing one molecule of He and one molecule of $\text{Fe}(\text{CO})_5$ didn't show noticeable deviation from corresponding equilibrium values. Simulation for the case 1% of $\text{Fe}(\text{CO})_5$ and $M=3.5$ had shown that MO is about 10^7 for GH .

However, to estimate the real contribution of such collisions in non-equilibrium excitation one should consider a dependence of inelastic interaction cross-section on collision energy. Note that for most systems probability of non-elastic transitions in collisions with energy above 3 eV amounts to $10^{-4} - 10^{-5}$ [9, 10].

3 Experimental results

Measurements were carried out in the mixtures containing 0.5-2.0% $\text{Fe}(\text{CO})_5$ in argon or helium at a rather low intensity of shock waves (Mach numbers from 2 up to 4) at which the equilibrium temperature T_2 behind the shock wave was less than 1500 K. At these temperatures no equilibrium radiation of any impurity could be expected. Nevertheless, optical measurements have recorded intense peaks after shock wave arrival in the mixtures containing $\text{Fe}(\text{CO})_5$. The measured spectra of radiation were situated in the range 400–700 nm. These spectra had unresolved structure, which testified a complex structure of radiating molecules. The radiation appeared immediately at the moment of shock front arrival and lasted about 8–12 μs . Maximal intensity of radiation was approximately proportional to $\text{Fe}(\text{CO})_5$ concentration and demonstrated strong dependence on carrier

gas molecular weight – intensity of radiation in helium was approximately ten times higher than in argon. Temperature dependence of intensity could be well described by the straight line, plotted through normalized experimental data presented in so-called ‘Boltzmann coordinates’. Notably, the effective energy of ionization derived from the slope of this dependence was essentially lower than the effective energy for radiation excitation and amount only ~ 1.1 eV.

Performed estimations have shown, that obtained data could not be satisfactory explained by the model of high-energy collisions in a shock front.

4 Results of kinetic modeling

According to the results [7] it was assumed that the registered radiation arises due to nonequilibrium energy release at the fast recombination of metal atoms formed as a result of immediate decay of $\text{Fe}(\text{CO})_5$ molecules behind the shock wave front.

For a detailed description of the observed phenomena the numerical modeling based on the latest kinetic mechanisms of the kinetics of $\text{Fe}(\text{CO})_5$ decomposition and the following iron cluster formation [11,12] has been carried out. These mechanisms consider several blocks of reactions — decomposition of $\text{Fe}(\text{CO})_5$ molecules, formation and decomposition of small iron clusters and coagulation of clusters.

An immediate rise in the radiation intensity after the shock wave arrival allows us to assume that radiation originates from the smallest iron clusters, containing several Fe atoms. Therefore, the detailed kinetic scheme was supplemented with two additional sets of reactions describing the formation and quenching of small excited clusters Fe_2 – Fe_9 .

The threshold of the process of excited cluster formation was assigned to be equal to the difference in the energy of radiation quantum and the energy of the forming bond. The absolute values of the rates of excited cluster formation, determined by the pre-exponent factor A , were chosen to be significantly less than the rates of non-excited cluster formation in order to avoid the influence of these new sets of reactions on the general kinetics of cluster formation in the temperature range investigated in [11]. The quenching of excited iron clusters was described based on the recent data on thermal energy accommodation coefficients in collisions of Ar and He atoms with iron nanoparticles [13]. These values, extracted from LII measurements, testify that quenching by He is about 10 times less effective than by Ar, i.e. $k_q(\text{He}) \approx 0.1 k_q(\text{Ar})$. Absolute values of the quenching reaction rates were derived from cluster geometric cross-sections.

Calculations were performed using the standard CHEMKIN II soft package. The intensity of the observed radiation was estimated to be proportional to the summary concentration of excited clusters Fe_2^* – Fe_9^* . It was shown that the maximum concentration of the excited particles is attained less than $1\mu\text{s}$ after the shock wave front arrival, and the increase in the peak of radiation in helium against argon is in a good agreement with the experimental observations. Results of modeling also perfectly reproduce the experimentally observed temperature dependence of radiation intensity.

5 Conclusion

The performed estimations have shown that experimentally observed intensive non-equilibrium effects in mixtures containing about 1% $\text{Fe}(\text{CO})_5$ in an inert gas could not be explained in high-energy collisions approach convincingly and predominantly originated by the rapid exothermic processes of iron clusters growth. Developed kinetic model proved that characteristic times of that process are very short (and, thus, can't be resolved with any convenient shock tube diagnostic methods) and successfully explain the increasing of observed signals in the lightweight carrier gases by the less efficiency of the quenching collisions of excited particles with the lighter molecules.

For further investigation of possible effects, caused by high-energy collisions in a shock wave front, the additional high-sensitive measurements in the mixtures containing less than 0.1% $\text{Fe}(\text{CO})_5$, where the processes of cluster growth could be neglected, are required.

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