SHOCK WAVE PROPAGATION IN GASEOUS MEDIA WITH MOLECULE DECOMPOSITION FOLLOWED BY FRAGMENT CONDENSATION

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Shock wave propagation in reactive media results in chemical transformation which in its turn influences the shock wave parameters. In the case of overall endothermic chemical process one can refer to accompanying problems of shock wave instability [1] and abnormal relaxation [2, 3]. Further insights into the subject can be gained by studying chemically well defined systems both experimentally and theoretically.

In this paper we report on the results of studying shock wave propagation in argon with Fe(CO)₅ additive. Kinetics of Fe(CO)₅ decomposition and subsequent condensation of Fe vapor were studied earlier in [4, 5]. The most remarkable feature of the process is its sign variable thermal effect. In fact, the first step Fe(CO)₅ decomposition to Fe atoms and CO molecules results in heat absorption, while the subsequent condensation of Fe vapor results in heat release, so that the overall thermal effect of the process is negative. Mixture cooling at the decomposition stage and heating at the condensation stage depends on a molar fraction of Fe(CO)₅ in a mixture.

In experiments we used argon-diluted mixtures containing 0.3% to 20% Fe(CO)₅. Experiments have been carried out by the use of two stainless steel shock tubes 38 and 75 mm in diameter, 3 and 4.5 m long respectively. Shock wave velocity was determined by the use of four flush mounted pressure transducers.

In calibration runs with pure argon continuous slight decrease in shock velocity has been registered. However, at Fe(CO)₅ concentrations exceeding 0.3% vol. we observed shock wave acceleration. Table shows the scope of experimental data (V is the shock velocity, ΔV the shock velocity increment).

A mathematical model of the shock wave propagation has been suggested. The chemical process is modelled by a set of two coupled reactions

\[ \text{Fe(CO)}_{5} \rightarrow 5\text{CO} + \text{Fe} + Q_{1} \]

\[ m\text{Fe} \rightarrow \text{condensate} + Q_{2} \]

with the corresponding kinetic equations

\[ \frac{d[\text{Fe(CO)}_{5}]}{dt} = -k_{1}[\text{Fe(CO)}_{5}][M] \]

\[ \frac{d[\text{Fe}]}{dt} = k_{1}[\text{Fe(CO)}_{5}][M] - k_{2}[\text{Fe}]^{2} \]
where \( Q_1 \) and \( Q_2 \) are the thermal effects of the stages, \( k_1 = \frac{[M]10^{14}\exp(-30000/RT) \text{ sec}^{-1} \), \( k_2 = \eta(T)10^5 \text{ m mole sec}^{-1} \), \( \eta(T) \) is the function of temperature reflecting specific features of nucleation process.

The analysis of a quasistationary problem allowed to interpret processes behind a shock wave in the 'pressure - specific volume' plane and put forward a mechanism responsible for shock acceleration at slow reaction kinetics.

The treatment of nonstationary problem confirmed qualitative conclusions based on the quasistationary solution. It is shown that the observed shock acceleration can be explained in terms of shock tube operation principles, namely, by the constant velocity of a driver gas - test gas contact surface in experimental conditions.

REFERENCES


Table. Measured velocity increments of a shock wave propagating in Ar + Fe(CO)_5 mixtures

<table>
<thead>
<tr>
<th>Fe(CO)</th>
<th>( \Delta V_{12} ) *</th>
<th>( \Delta V_{12} )</th>
<th>( \Delta V_{23} ) **</th>
<th>( V_{12}, V_{23} )</th>
<th>( \Delta V/V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>m/s</td>
<td>m/s</td>
<td>m/s</td>
<td>m/s</td>
<td>%</td>
</tr>
<tr>
<td>0.3</td>
<td>+3.5(29)***</td>
<td>-</td>
<td>-</td>
<td>1200</td>
<td>+0.3; -</td>
</tr>
<tr>
<td>1.0</td>
<td>+25(32)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+2.0; -</td>
</tr>
<tr>
<td>3.0</td>
<td>+38(22)</td>
<td>+17(5)</td>
<td>+34(5)</td>
<td>-</td>
<td>+3.2; +4.3</td>
</tr>
<tr>
<td>10.0</td>
<td>-</td>
<td>+30(7)</td>
<td>+51(7)</td>
<td>-</td>
<td>+6.8</td>
</tr>
<tr>
<td>20.0</td>
<td>-</td>
<td>+198(5)</td>
<td>+52(5)</td>
<td>-</td>
<td>+21</td>
</tr>
</tbody>
</table>

* Measured in a shock tube 75 mm in diameter, low pressure chamber 3 m long, high pressure chamber 1.5 m long; measuring bases: \( \Delta l_{12} = 528 \text{ mm}, \Delta l_{23} = 280 \text{ mm} \)

** Measured in a shock tube 38 mm in diameter, low pressure chamber 2 m long, high pressure chamber 1 m long; measuring bases: \( \Delta l_{12} = \Delta l_{23} = 300 \text{ mm} \)

*** Shown in brackets is the number of runs used in averaging procedure

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