Theory of Solid-State Detonation

L. G. Bolkhovitinov\(^1\) and S. S. Batsanov\(^1\)  

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The Jouguet theory allows one to estimate the detonation velocity from the known shock adiabat of the product of a solid-state chemical reaction initiated by a shock wave. Using manganese and zinc chalcogenides as an example, it is shown that such estimates are close to experimental detonation velocities in these systems.  

Key words: detonation, shock adiabat, Hugoniot equation, solid, heat.

Bennet and Horie\([1]\) considered the problem of gasless detonation for the Ni–Al system, in which shock compression initiates an exothermic reaction with increasing volume. Calculations of the Hugoniot equations for this mixture using the constant-pressure scheme indicate the possibility of a self-sustained reaction (detonation) proceeding in the condensed state. Gordopolov et al.\([2]\) proposed a criterion for the possibility of solid-state detonation occurring in the case where the exothermic reaction proceeds with increasing volume at constant pressure and enthalpy. In the present paper, this problem is solved using the classical Jouguet–Zel’dovich theory, in which the hydrodynamic equations describe the state of the medium in the Jouguet plane, where the chemical reaction is terminated.  

As is known, the relations for the mass, momentum, and energy fluxes, the equation of state for the medium behind the shock, and the Chapman–Jouguet condition, according to which the shock velocity is equal to the sum of the particle velocity behind it \(u_j\) and the local sound velocity \(c_j\), form a system of equations that allows one to determine all state parameters behind the shock from the characteristics of the initial state of medium and the heat of the reaction.  

For gases, \(c^2 = \gamma pV\) and \(H = c^2/(\gamma - 1)\) (\(\gamma\) is the ratio of the heat capacities, \(p\) is the pressure, \(V\) is the specific volume, and \(H\) is the enthalpy). After simple manipulations, the detonation theory gives the following expression for the velocity of a strong discontinuity \(D\) in gas mixtures:

\[
D^2 = 2(\gamma^2 - 1)(H_0 + q).
\]

Here \(H_0\) is the enthalpy in the initial state, \(q\) is the heat of the chemical reaction, defined as the difference of the standard heats of formation of the starting mixture of substances and the reaction products. We note that Eq. (1) was derived under the assumption that one can ignore the initial pressure in the relation for the momentum flux

\[
p_0 + \rho_0 D^2 = p_j + \rho_j(D - u_j)^2
\]

\((\rho_0\) and \(\rho_j\) are the initial and current densities).  

A difficulty in the application of the Jouguet theory to the detonation of condensed explosives was the absence of equations of state for reaction products in the form of dense gases. In 1945, Landau and Stanyukovich\([3]\) paid attention to the fact that at a gas density \(\approx 2\) g/cm\(^3\), the motion of gas molecules reduces to small vibrations about the time equilibrium position. The statistical sum in this case is the same as for solids. They further suggested that the pressure is determined primarily by repulsive forces and, hence, can be represented as \(p = Ap^n\), where \(\rho\) is the density and \(n\) is the exponent of the repulsive-force potential. In this case, the expressions for the sound velocity and enthalpy are written as

\[
c^2 = npV;
\]

\[
H = -\int pdV + pV = \frac{A}{(n - 1)V^{n-1}} + pV
\他也 greater than or equals
\[
= \frac{n}{n - 1} pV = \frac{c^2}{n - 1}.
\]

\(^1\)Center of High Dynamic Pressures, National Research Institute of Physicotechnical and Radiotechnical Measurements, Mendeleeevo 141570; batsanov@gol.ru.
Since these relations coincide with the same expressions for gases, the formal apparatus of the theory developed for gases is automatically extended to the detonation of condensed systems by replacing \( \gamma \) by \( n \).

It seems obvious that the arguments of Landau and Stanyukovich also apply to the case where the reaction product is a solid. In this case, the detonation velocity can be obtained from formula (1) provided the value of \( n \) is determined from physical considerations. Thus, one can set \( n = 3 \) if the reaction products are identified with Landau gas, or \( n = 4 \) if the Lennard-Jones potential is used. To determine \( n \), we use the following circumstance.

In the case considered, because the chemical-reaction products are solids, their properties can be studied by ordinary methods, having determined, in particular, the relation between the shock velocity \( D \) and the particle velocity \( \rho \), which in the overwhelming number of cases has the form

\[
D = a + bu. \tag{3}
\]

The volume of the shock-compressed material is given by

\[
\frac{V}{V_0} = 1 - \frac{U}{D} = 1 - \frac{D - a}{bD} = \frac{b - 1}{b} + \frac{a}{bD}.
\]

The value of the volume for the limiting compression is obtained for \( D \to \infty \):

\[
\frac{V_{\text{lim}}}{V_0} = \frac{b - 1}{b}. \tag{4}
\]

Assuming, according to Stanyukovich and Landau, that the pressure (and hence, energy) depends only on repulsive forces, and substituting the enthalpy (2) into the shock adiabat equation

\[
\frac{n}{n - 1} pV - H_0 = \frac{1}{2} (p + p_0)(V_0 - V),
\]

after simple transformations, we obtain the value of the limiting volume \( V_{\text{lim}} \) for \( p \to \infty \):

\[
\frac{V_{\text{lim}}}{V_0} = \frac{n - 1}{n + 1}. \tag{5}
\]

Combining Eqs. (4) and (5), for the adopted pressure-density relation we obtain

\[
n = 2b - 1. \tag{6}
\]

Because \( D - u_j = c_j \) according to the Chapman–Jouguet condition, the continuity equation implies

\[
\frac{p_0}{\rho_j} = \frac{c_j}{D}
\]

and

\[
c_j = \frac{n}{n + 1} D.
\]

Substituting this value of the sound velocity into the energy flux equation, we write

\[
H_0 + q + \frac{D^2}{2} = \frac{(n + 1)n^2}{2(n - 1)(n + 1)^2} D^2,
\]

whence

\[
D^2 = 2(n^2 - 1)(H_0 + q),
\]

i.e., we obtain the formula that coincides with (1) if \( \gamma \) is replaced by \( n \). Finally, substitution of the quantity \( n \) with the value taken from (6) into the latter expression gives

\[
D^2 = 2[(2b - 1)^2 - 1](H_0 + q). \tag{7}
\]

To date, studies have been made of shock-induced exothermic solid-state synthesis reactions of zinc and manganese chalcogenides proceeding with increasing volume. Detonation velocities calculated by formula (7) (in the calculation, \( H_0 \ll q \)) are listed in Table 1. For ZnS, the shock adiabat and, hence, the value of \( b \) are known [4]. For ZnTe and MnS, experimental shock adiabats are not available and the values of \( b \) are calculated by the formula \( b = 0.25(B'_0 + 1) \), where \( B'_0 \) is the first derivative of the bulk elastic modulus with respect to pressure [5]. The values of the heat effects of the reactions are taken from [6].

Taking into account the ordinary divergences in the experimental determination of the values of the factor \( b \) in Eq. (3), the results of calculations of solid-state detonation velocities by formula (7) should be regarded as an estimate close to experimental data.

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**REFERENCES**


**TABLE 1**

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>( b ) (product)</th>
<th>( q ), kJ/g</th>
<th>( D ), km/sec</th>
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</thead>
<tbody>
<tr>
<td>Zn + S</td>
<td>1.30</td>
<td>2.10</td>
<td>2.56</td>
</tr>
<tr>
<td>Zn + Te</td>
<td>1.45</td>
<td>0.62</td>
<td>1.80</td>
</tr>
<tr>
<td>Mn + S</td>
<td>1.30</td>
<td>2.46</td>
<td>2.77</td>
</tr>
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