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Abstract

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On the Detonation of Liquid Explosives at Low Velocity

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It is known that in certain liquid explosives (nitroglycerin, methyl nitrate), alongside the normal detonation regime, whose velocity is equal to 7-8 km/sec and corresponds to their thermochemical characteristics, a regime can occur to which there corresponds a propagation velocity of only 1.7-2.2 km/sec ($^{1-4}$). The main difficulty in explaining this phenomenon is that, at a low shock-wave velocity close to the speed of sound (approximately 1.5 km/sec), the temperature increase upon compression in the wave is small and cannot initiate a chemical reaction in the substance.

Indeed, an estimate of the temperature rise from the relation

$$\Delta T \simeq (D - c)^2 / 2c_v \qquad (1)$$

gives, for liquids at $c \simeq c_0 = 1.5$ km/sec, $c_v = 0.3$ cal/g deg and $D = 2$ km/sec, $\Delta T \simeq 100°$.

Therefore Boden' s assumption (^{5}), that the reaction begins at sites of gas inclusions, which upon compression are heated much more strongly than the main mass of the explosive, is generally accepted. It is also assumed that the small value of the detonation velocity is associated with incomplete decomposition of the substance owing to the expansion of the reaction products. This assumption, however, does not explain the fact that the low detonation velocity, like the normal velocity, is practically independent of the charge diameter, whereas the expansion time of the detonation products is related precisely to the charge diameter. It also remains unclear why no detonation regimes are observed to which velocities of 3-7 km/sec would correspond.

It seems to us that this phenomenon can be interpreted very simply if one starts from the experimentally discovered fact that the passage of a shock wave through a substance may be accompanied by phase transformations (^{6},^{7}). The phase transformation that may accompany the passage of a shock wave through a liquid explosive is crystallization. Since within the shock-wave front, whose width is only several intermolecular distances, a phase change cannot occur, the transition of the liquid into the crystalline state must take place in some zone behind the shock-wave front, the width of which is determined by the crystallization rate of the explosive.

The possibility of formation of this zone is connected with the mutual arrangement of the phase-equilibrium curve and the curve $T = f(\Delta p)$, which describes the temperature increase behind the shock-wave front as a function of the pressure jump. For illustration, Fig. 1 shows the phase-equilibrium curves of two liquids (1 and 2) and the curve $T = f(\Delta p)$ common to them (3). It is evident that an increase of pressure in the shock wave to values p, $p_a < p < p_b$, should lead to the appearance of a crystallization zone in liquid 1, whereas in liquid 2 a crystallization zone does not arise at any shock-wave intensity.

Let us consider the change in pressure p, specific volume $v \equiv \frac{1}{\rho}$, and flow velocity w on both sides of the crystallization zone. Let us denote by indices

0, 1, and 2 are the quantities, respectively, in the undisturbed substance, at the shock-wave front, and in the plane in which the phase transformation has been completely completed. The conservation laws give two systems of equations:

$$\rho_0 D = \rho_1 (D - w_1); \tag{2}$$

$$\rho_0 w_1 D = p_1; \tag{3}$$

$$H_1 - H_0 = p_1 \frac{v_1 + v_0}{2} \tag{4}$$

and, correspondingly,

$$\rho_0 D = \rho_2 (D - w_2); \tag{5}$$

$$\rho_0 w_2 D = p_2; \tag{6}$$

$$H_2 - H_0 = p_2 \frac{v_2 + v_0}{2} \tag{7}$$

(we assume that $p_1 \gg p_0$). From equations (4) and (7) it follows that

$$2(H_2 - H_1) = v_0 (p_2 - p_1) + p_2 v_2 - p_1 v_1. \tag{8}$$

The quantity $p_2 - p_1$ is found from (2), (3), (5), and (6):

Fig. 1. Possible relations between the curves of phase equilibrium (1 and 2) and the state of the substance behind the shock-wave front (3)

Figure 1: Fig. 1. Possible relations between the curves of phase equilibrium (1 and 2) and the state of the substance behind the shock-wave front (3)

$$p_2 - p_1 = \rho_0^2 D^2 (v_2 - v_1). \tag{9}$$

If the change in the quantity v due to compressibility when the pressure changes from p_1 to p_2 is neglected in comparison with the change in volume during the phase transformation, then one may put $v_2 - v_1 = \Delta v_\phi$, where Δv_ϕ is the jump in volume upon change of phase. Rewriting (8) in the form

$$2(H_2 - H_1) = v_0(p_2 - p_1) + v_1(p_2 - p_1) - p_1(v_2 - v_1)$$

and using (2), (3), and (9), we obtain

$$(H_2 - H_1) = \frac{\Delta v_\phi v_1}{v_0^2} D^2.$$

Assuming that the change in enthalpy in going from state 1 to state 2 is simply equal to the latent heat of fusion λ, we obtain from the last equation

$$D = \left[\frac{\lambda v_0^2}{\Delta v_\phi v_1}\right]^{1/2}. \tag{10}$$

If in the $p - v$ plane one plots (see Fig. 2) the Hugoniot adiabat for the initial substance, then the state at point A, corresponding to compression in a strong wave, is realized in detonation with the normal velocity D_n. Point B corresponds to the state 2 considered above; moreover, the slope of the straight line OB is given, and, consequently, the magnitude of the small velocity D_m is determined by relation (10). If one assumes that the crystallization zone is followed by a chemical-reaction zone with a normal structure (which is true only insofar as we may neglect the chemical reaction in the first zone), then the pressure in the Chapman—Jouguet plane must be equal to $0.5\,p_2$. This pressure in the $p - v$ diagram (curve 1) corresponds to the point of tangency of the straight line OB not with the isentrope of the reaction products 2, but with a certain curve 3, which is an isentrope of only partially reacted substance. In other words, a low detonation velocity can be realized only when the expansion time of the reaction products is comparable with the time of the chemical reaction.

Since, for the stationary propagation of a detonation wave, it is necessary that the well-known condition of Yu. B. Khariton, $\tau \ll \Theta$, be fulfilled, where τ –

Fig. 2. p–v diagram for detonation with normal and low velocity

Figure 2: Fig. 2. p–v diagram for detonation with normal and low velocity

Fig. 1. Possible relations between the curves of phase equilibrium (1 and 2) and the state of the substance behind the shock-wave front (3).

the time of the chemical reaction (more precisely, the time of release of the energy necessary to maintain the stationary wave), and Θ is the time of expansion of the reaction products, then the appearance behind the shock wave of a crystallization zone leads to a sharp increase in the scatter time and, consequently, Yu. B. Khariton’ s condition may also be satisfied at large τ. This follows from the fact that the speed of sound in a two-phase system decreases in comparison with the speed of sound in a liquid (^{8}). Therefore it is not immaterial whether the temperature rises to a certain value T by direct compression in the shock wave (without the appearance of a crystallization zone) or by means of the mechanism we propose. In the first case the expansion of the substance begins immediately behind the shock wave, whereas in the second only when, as a result of the chemical reaction, the difference between the solid and liquid phases disappears. This, in our opinion, explains the stability of detonation with a low velocity, in contrast to regimes with high propagation velocities but not accompanied by crystallization.

Fig. 2. p–v diagram for detonation with normal and low velocity

As an example let us consider detonation with low velocity in nitroglycerin ($T_{\text{m}} = 13.2^\circ$), for which the heat of fusion and the change in volume upon solidification are known (^{9}). Substituting in (10) the values $\lambda = 33.2$ cal/g, $v_0 = 0.62$ cm^3/g and $\Delta v_\phi = 0.05$ cm^3/g, we find that when the value of v_1 changes from v_0 to $0.5v_0$ the velocity of the stationary shock wave changes from 1310 to 1830 m/sec. Since we used the values of λ and Δv_ϕ measured at atmospheric pressure, whereas in the wave crystallization occurs at a pressure varying from p_1 to p_2, the velocity obtained is underestimated (by up to 30%), because with increasing pressure the heat of fusion increases and Δv_ϕ decreases (^{10}). Taking this into account, the value of D calculated by us may be regarded as in good agreement with the experimental results.

If it is assumed that the isentrope equation for the products of incomplete decomposition of the explosive can be written in the form proposed by L. D. Landau and K. P. Stanyukovich: $pv^n = \text{const}$, and that the value of n may be taken equal to 3, then from the condition $p_2 = 2\rho_0 D^2/(n+1)$ we obtain that, for $D = 1700$ m/sec, $p_2 = 24000$ atm and $p_1 = 19500$ atm. For a wave velocity $D = 2000$ m/sec we obtain, respectively, $p_2 = 32000$ atm and $p_1 = 26000$ atm. Estimation of the temperature of the phase transition at these pressures from the Clapeyron-Clausius equation, or by analogy with Bridgman’ s experimental data (^{10}) for high-molecular organic compounds, gives a temperature in the crystallization zone equal to 450-600°. An increase in the temperature of the explosive to the cited value can indeed ensure that the chemical reaction proceeds at the required rate.

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