

Calculation of the Detonation Properties of Solid Explosives with the Kistiakowsky-Wilson Equation of State*

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The Kistiakowsky-Wilson equation of state, $pV_g = RT(1 + \alpha x e^{\beta x})$, where $x = k/V_g(T + \theta)^\alpha$, for the gaseous detonation products of solid explosives has been re-examined in the light of new experimental data on detonation pressure and on the variation of detonation velocity D with loading density ρ_0 for several RDX/TNT mixtures. The value $\beta = 0.30$ used in the past is too high to match the observed slopes of the $D - \rho_0$ curves. The old value $\alpha = 0.25$ is too small to match the experimental Chapman-Jouguet pressure of most of these explosives, but too large to match the pressure of pure TNT. A suitable compromise for the explosives considered is $\alpha = 0.5$, $\beta = 0.09$, $\theta = 400^\circ\text{K}$.

1. INTRODUCTION

A NUMBER of attempts have been made in the past to calculate the detonation properties of solid explosives.¹⁻¹² Since the gaseous detonation products develop pressures of the order of a quarter megabar ($1 \text{ Mb} = 10^{12} \text{ dynes/cm}^2 = 0.98692 \times 10^6 \text{ atmos}$), directly applicable equation-of-state data are non-existent and some form of theoretical or empirical equation of state for the detonation products must be assumed. When the investigations quoted in the aforementioned were made the only reliable experimental data available for comparison with the calculated results were detonation-velocity measurements; such data do not provide a very sensitive test of the correctness of the assumed equation of state. Recently, however, accurate measurements of the detonation pressures of several explosives have been made at this laboratory.^{13,14} We have employed this data in a reinvestigation of an empirical equation of state which was first proposed by Kistiakowsky, Wilson, and Halford⁵ and which has been utilized extensively for detonation calculations.⁵⁻¹²

The Kistiakowsky-Wilson equation of state as

slightly modified by us has the form

$$pV_g/RT = F(x) = 1 + \alpha x e^{\beta x}, \quad (1)$$

where

$$x = k/V_g(T + \theta)^\alpha, \quad k = \sum_i x_i k_i.$$

Here V_g is the molar gas volume, x_i is the mole fraction of component i , and the sum extends over all chemical components of the gaseous mixture. The quantities α , β , κ , θ , k_i are empirical constants, the k_i having the nature of covolumes (i.e., a sort of excluded volume) as is shown by the equilibrium equation (5). The values $\alpha = 0.25$ and $\beta = 0.30$, which were chosen originally⁵ to give agreement with the experimental data then available, have been used in all of the succeeding work with this equation of state. However, several different sets of values of the k_i have been determined from experimental data (see references 9-11 and 12). We have treated all of the parameters (α , β , κ , k_i 's) as adjustable in an effort to determine a set which would make it possible to match a set of experimental data which includes both the variation of detonation velocity with loading density ($D - \rho_0$), and the Chapman-Jouget pressure (p_{CJ}) at high loading density for a group of five related explosives.

With the value $\theta = 0$ which has been used in the past, it may easily be seen that the equation of state has a minimum in p vs T (for constant V_g and composition). With $\alpha = 0.25$ and with values of V_g appropriate to the detonation region this minimum occurs near 0°K , but with $\alpha = 0.5$ it moves up to 2000 or 3000°K . We have used the arbitrary value $\theta = 400^\circ\text{K}$ for all values of α ; this has proved to be large enough to eliminate the minimum throughout the volume region characteristic of plane detonations, and yet is small compared with the values of T encountered.

The calculations are complicated by the possible presence of solid carbon. We have assumed this to be present as graphite and treated its equation of state as known, using a form employed extensively at this laboratory:

$$p = p_1(V_s) + a(V_s)T + b(V_s)T^2, \quad (2)$$

where, with p in megabars and T in volts (i.e., in units

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