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An Equation of State for Gases at Extremely High Pressures and Temperatures from the Hydrodynamic Theory of Detonation

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The hydrodynamic theory of detonation is derived in a convenient form for practical utility by employing the general equation of state $p v = n R T + \alpha(T, v) p$. Two methods of solution of the general equations based on measured detonation velocity are discussed. In method (a) the detailed form of $\alpha(T, v)$ is unspecified. It is therefore, in principle, at least, a general solution. However, in practice one finds that it is impossible due to the experimental error in detonation velocities to evaluate the heat capacity at constant volume and hence the detonation temperature without specifying a particular form of $\alpha(T, v)$. The postulate (used only in the calculation of temperature) is $\alpha = \alpha(v)$. Method (b) employs the approximation $\alpha = \alpha(v)$ throughout. Methods (a) and (b) lead to identical results

which one will find in view of the comparative nature of the two methods, is good evidence (but not conclusive proof) for the validity of the above approximation. This is supported also by the discovery that the same α vs. v_2 curve applies to all explosives yet considered. As a matter of fact, it has been found that the detonation velocities may themselves be computed within experimental error, evidently for explosives of all types (where sufficient heat data are available) by employing the $\alpha(v)$ function evaluated from a few selected explosives. Several additional arguments supporting the above approximation are discussed. Data on the detonation properties of several explosives are presented and correlated with similar data obtained by other investigators.

INTRODUCTION

THE hydrodynamic theory of detonation developed by Chapman,² Jouguet,³ Becker,⁴ Schmidt,⁵ and others has recently been carefully scrutinized and extended by various investigators including Landau and Stanyukovich,⁶ Ratner,⁷ Kistiakowsky and Wilson,⁸ von Neumann,⁹ Brinkley and Wilson,¹⁰ Eyring and collaborators,¹¹ and others. In the application of the hydrodynamic theory of detonation to condensed explosives a particular form of the equation of state is generally assumed and the parameters are evaluated experimentally through the hydrodynamic theory, by introducing measured deto-

nation velocities. Consequently, the theory has not yet been demonstrated for condensed explosives as directly as might be desired, although much convincing indirect evidence is available and the general validity of the theory is unquestioned at the present time. The objectives of the present study are (1) to derive the theory for condensed explosives in a useful form, (2) to show how the theory and measured velocities may be used to derive an equation of state applicable in the study of other detonation and high pressure phenomena, and (3) to discuss some interesting features of the derived equation of state.

DERIVATION OF EQUATION

The fundamental equations of the hydrodynamic theory of detonation are

$$D = v_1((p_2 - p_1)/(v_1 - v_2))^{1/2}, \quad (1)$$

$$W = (v_1 - v_2)((p_2 - p_1)/(v_1 - v_2))^{1/2}, \quad (2)$$

$$E_2 - E_1 = \frac{1}{2}(p_2 + p_1)(v_1 - v_2), \quad (3)$$

$$(p_2 - p_1)/(v_1 - v_2) = -(\partial p_2 / \partial v_2)_S. \quad (4)$$

Equation 3 is the Rankine¹²-Hugoniot¹³ adiabatic (or "dynamic adiabatic") relation. Equation (4)

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is equivalent to the Chapman-Jouguet postulate

$$D = W + C. \quad (5)$$

Here D is the detonation velocity; W and C are the particle and sound velocities, respectively, in the medium (products of detonation) immediately behind the wave front; v , p , and T are the state variables; E is the total energy and S the entropy. The subscript 1 refers to the thermodynamic quantities in the undetonated explosive, and the subscript 2 to the corresponding quantities in the medium immediately behind the shock front (where the Chapman-Jouguet condition applies).

For a solution of the above equations, the following general equation of state is adopted

$$pv = nRT + \alpha(T, v)p. \quad (6)$$

To derive an expression for $(\partial p_2 / \partial v_2)_S$ the following thermodynamic equation for an adiabatic equilibrium process is used:

$$-C_v \partial T_S = ((\partial E / \partial v)_T + p) \partial v_S. \quad (7)$$

Differentiating Eq. (6), solving for ∂T_S , and introducing the result into Eq. (7) gives

$$-(\partial p_2 / \partial v_2)_S = p_2 \beta / (v_2 - \alpha), \quad (8)$$

where

$$\beta = (nR + C_v) / C_v - (\partial \alpha / \partial v_2)_S + (\partial E / \partial v)_T nR / C_v p_2. \quad (9)$$

Here C_v is the heat capacity at constant volume (per kilogram), R is the gas constant, and n the number of molecules of gas per kilogram. The subscript 2 is introduced to show that Eqs. (8) and (9) apply immediately behind the wave front.

By employing Eqs. (4), (6), and (8), Eq. (1) becomes

$$D^2 = v_1^2 p_2 \beta / (v_2 - \alpha) = v_1^2 (nRT_2 \beta) / (v_2 - \alpha)^2. \quad (10)$$

Since $p_2 \gg p_1$ in condensed explosives, Eqs. (4) and (8) give

$$\beta = (v_2 - \alpha) / (v_1 - v_2). \quad (11)$$

Combining Eqs. (1) and (6), the equation

$$(v_2 - \alpha)(v_1 - v_2) = v_1^2 (nRT_2) / D^2 \quad (12)$$

is obtained. The equation

$$\alpha = v_1 - v_1(\beta + 1)(nRT_2)^{1/2} / D\beta^{1/2} \quad (13)$$

may then be derived from Eqs. (10) and (11).

Similar substitutions in Eqs. (2) and (3) give

$$W = (nRT_2 / \beta)^{1/2}, \quad (14)$$

and

$$E_2 - E_1 = nRT_2 / 2\beta. \quad (15)$$

The detonation temperature is then given by

$$T_2 = (Q + T_1 \bar{C}_v) \beta / (\beta \bar{C}_v - \frac{1}{2} nR), \quad (16)$$

where Q is the chemical energy released in detonation (the heat of explosion), and $\bar{C}_v$ is the average heat capacity at constant volume (v_2) between T_2 and T_1 .

SOLUTION OF EQUATIONS

Either of two quite different methods of solution of the above equations may be used, both of which will be discussed since they prove to be complementary in providing information on the nature of the equation of state.

(a) The first method is a solution in which the detailed form of β is not taken into account. This solution is made possible by the fortuitous cancellation of p_2 in obtaining Eq. (11). The Eqs. (11), (12), (13) and (16) may be solved by successive approximations employing a measured value of D at any given density (ρ_1). A value of β is selected and T_2 calculated from Eq. (16). (In the calculation of T_2 , the low density value of $\bar{C}_v$ has been used as discussed below. This is equivalent to the approximation $\alpha = \alpha(v)$ which was used in method (a) only in the evaluation of T_2 . This approximation or an equivalent one is necessary because of the experimental error in measured detonation velocity, making a reliable evaluation of $\bar{C}_v$ impossible.) Equation (13) is used to evaluate α , and v_2 is obtained from (12) for these values of α and β . Equation (11) may then be used to check β . If this value of β does not agree with the selected value, the approximations are repeated until the successive β 's converge to a constant value. It is here tacitly assumed that n , Q , and $\bar{C}_v$ are known. Actually they must also be evaluated by thermodynamic methods and, in view of their dependence on v_2 , T_2 , and α , they must be re-evaluated in each successive approximation unless, as is the case in the final approximations, they do not vary appreciably. As a matter of fact the approximations converge quite rapidly since α obtained