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

#### INTRODUCTION

HE hydrodynamic theory of detonation developed by Chapman,<sup>2</sup> Jouguet,<sup>3</sup> Becker,<sup>4</sup> Schmidt,<sup>5</sup> 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,<sup>9</sup> Brinkley and Wilson,<sup>10</sup> Eyring and collaborators,<sup>11</sup> 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-

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  $\alpha$  vs. v<sub>1</sub> 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.

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

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

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

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

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

Equation 3 is the Rankine<sup>12</sup>-Hugoniot<sup>13</sup> adiabatic (or "dynamic adiabatic") relation. Equation (4)

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<sup>&</sup>lt;sup>2</sup> D. Chapman, Phil. Mag. 47, 90 (1899).

<sup>&</sup>lt;sup>3</sup> E. Jouguet, J. de math. 1, 347 (1905); 2, 1 (1906).

<sup>&</sup>lt;sup>4</sup> R. Becker, Zeits. tech. Physik 8, 152, 249 (1917), 8, 321 (1922).

<sup>&</sup>lt;sup>5</sup> A. Schmidt, Zeits. f. das gesamte Schiess u. Sprengstoff-

 <sup>&</sup>lt;sup>6</sup>L. Landau and K. Stanyukovich, comptes rendus (URSS) 36, 362 (1945).

<sup>7</sup> S. Ratner, comptes rendus (URSS) 48, 187 (1945).

<sup>&</sup>lt;sup>8</sup>G. B. Kistiakowsky and E. B. Wilson, Jr., OSRD Report 69.

J. von Neumann, OSRD Report 549. 10 S. R. Brinkley, Jr. and E. B. Wilson, Jr., OSRD

Report 905. <sup>11</sup> H. Eyring, R. E. Powell, G. H. Duffey, R. B. Parlin, OSRD Report 3796.

<sup>12</sup> W. J. M. Rankine, Phil. Trans. 160, 277 (1870).

<sup>&</sup>lt;sup>13</sup> Hugoniot, J. de math. **3**, 477 (1887); J. de l'école Polytech. **57**, 3 (1887); **58**, 1 (1889).

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and

is equivalent to the Chapman-Jouguet postulate

$$D = W + C. \tag{5}$$

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

$$pv = nRT + \alpha(T, v)p. \tag{6}$$

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

$$-C_{v}\partial T_{s} = ((\partial E/\partial v)_{T} + p)\partial v_{s}.$$
(7)

Differentiating Eq. (6), solving for  $\partial T_s$ , and introducing the result into Eq. (7) gives

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

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

$$D^{2} = v_{1}^{2} p_{2} \beta / (v_{2} - \alpha) = v_{1}^{2} (n R T_{2} \beta) / (v_{2} - \alpha)^{2}.$$
(10)

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

$$\beta = (v_2 - \alpha) / (v_1 - v_2). \tag{11}$$

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

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

is obtained. The equation

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

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

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

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

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

The detonation temperature is then given by

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

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  $\beta$  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  $(\rho_1)$ . A value of  $\beta$  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  $\alpha$ , and  $v_2$  is obtained from (12) for these values of  $\alpha$  and  $\beta$ . Equation (11) may then be used to check  $\beta$ . If this value of  $\beta$  does not agree with the selected value, the approximations are repeated until the successive  $\beta$ 's converge to a constant value. It is here tacitly assumed that n, Q, and  $\overline{C}_v$  are known. Actually they must also be evaluated by thermodynamic methods and, in view of their dependence on  $v_2$ ,  $T_2$ , and  $\alpha$ , 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  $\alpha$  obtained

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from Eq. (13) is quite insensitive to different values of  $\beta$  and  $nT_2$ .

For evaluating the products of detonation a modification of the method developed by Brown<sup>14</sup> was employed together with heat data taken from Bichowski and Rossini,<sup>15</sup> and Schmidt.<sup>16</sup> In this modification the experimental equation of state was used in setting up more exact equilibrium equations and the final approximations employed activity or fugacity rather than partial pressures in the thermodynamic equilibrium constants.

In principle  $\bar{C}_v$  may be evaluated from the equation

$$\bar{C}_{v} = \bar{C}_{v}^{*} + \frac{1}{T_{2} - T_{1}} \int_{\infty}^{v_{2}} (\partial E/\partial v)_{T} dv$$
$$= \bar{C}_{v}^{*} + \frac{1}{T_{2} - T_{1}} \int_{\infty}^{v_{2}} (\phi_{2}^{2}/nR) (\partial \alpha/\partial T)_{v} dv, \quad (17)$$

where  $\bar{C}_v^*$  is the low density average (constant volume) heat capacity between  $T_2$  and  $T_1$ . It will be seen that  $(\partial \alpha / \partial T)_v$ , if not effectively zero, is exceedingly small relative to  $p_2$ . Because of the enormously high pressures occurring in detonation, however, it is quite impossible to evaluate reliably the last term of Eq. (17) directly from the hydrodynamic theory of detonation since the detonation velocity (although known to within about 3 percent) and the necessary heat data are not known accurately enough for this purpose.

In application of method (a) it will be assumed, therefore, that  $\bar{C}_v = \bar{C}_v^*$ . Several more or less indirect evidences justifying this assumption are discussed in this report. One argument is the following:

Hirschfelder and Roseveare<sup>17</sup> showed that for gases at sufficiently high temperature the internal energy is a linear function of density  $(\rho)$ . At low density  $(\partial E/\partial \rho)_T = -a(T)$ , where a(T) is the van der Waals constant (which decreases with increasing temperature). It will be assumed in view of the high detonation temperatures that the linear variation of E with  $\rho$  holds over the entire range from low density to  $v_2$ . Thus this approximation gives

$$\int_{-\infty}^{v_2} (\partial E/\partial v)_T dv \approx a(T)/v_2 < 8 \text{ kg cal./kg}$$

for the products of detonation of PETN at a density of 2.0 kg/L. On the other hand,

$$\begin{split} \bar{C}_{v}(T_{2}-T_{1}) &= \bar{C}_{v}^{*}(T_{2}-T_{1}) \\ &+ \int_{\infty}^{v_{2}} (\partial E/\partial v)_{T} dv \approx 1200\text{--}1700 \text{ kg cal./kg.} \end{split}$$

Hence, according to this method  $\bar{C}_{v} = \bar{C}_{v}^{*}$  within 0.5 percent at  $v_2 = 0.5$  L./kg. (Likewise, for use in the alternate method of solution, it may be shown according to this method for evaluating  $(\partial E/\partial v)_T$  that the neglect of the last term in Eq. (9) will incur an error of less than 0.1 percent in  $\beta$ .) Hirschfelder and Roseveare showed that the linear variation of E with  $\rho$  is valid at least up to 3000 atmos. even at much lower than detonation temperatures. The extension of this linear law to detonation pressures ( $\sim 200,000$  atmos.) involves, of course, a large extrapolation in  $p_2$ . However, further evidence for the approximate validity of the extrapolation will be found in the correlation of the results obtained by method (a) described above, with those obtained from method (b).

(b) This method involves the use of  $D(\rho_1)$ data, and the separate evaluation of each term of Eq. (9) for  $\beta$ , the last term in (9) being neglected following the reasoning already given. As a first approximation  $\alpha$  may be evaluated from Eq. (13) over a range of densities by taking  $\beta = (C_v + nR)/C_v$ or by simply assuming values of  $\beta$ . A plot of  $\alpha$ against  $v_2$  is then constructed and the slope taken at various points along the curve giving a series of values of  $(\partial \alpha / \partial v_2)_s$ . The values of  $\beta$  obtained by including the term from the first approximation are introduced back into Eq. (13) to obtain better values of  $\alpha$ , the quantity  $nT_2$  also being corrected according to its dependence on  $\beta$ ,  $v_2$ , and  $\alpha$ . This process is repeated until all parameters converge to constant values. As in method (a) this series of approximations also converges rapidly.

In evaluating  $\beta$  by means of the slope of the

<sup>&</sup>lt;sup>14</sup> F. W. Brown, "Theoretical Calculations for Explosives," U. S. Bur. of Mines Technical Paper No. 132. <sup>15</sup> F. R. Bichowski and F. D. Rossini, *Thermochemistry of* 

<sup>&</sup>lt;sup>15</sup> F. R. Bichowski and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Company, New York, 1936).

<sup>&</sup>lt;sup>16</sup> Á. Schmidt, Zeits. f. das gesamte Schiess u. Sprengstoffwesen 29, 259 (1934).

<sup>&</sup>lt;sup>17</sup> J. O. Hirschfelder and W. E. Roseveare, J. Phys. Chem. **43**, 15 (1939).

 $\alpha$ , v curve it was tacitly assumed that the entropy  $S_2$  is constant along the curve. At any density  $(\rho_1)$ ,  $dS_2/dv_2=0$  according to the Chapman-Jouguet postulate. In the approximation  $\alpha = \alpha(v_2)$ , therefore, the change in  $S_2$  along the curve should be zero. There is, of course, a sharp increase in the entropy across the shock front, i.e.,  $S_2 - S_1 \gg 0$ . Scorah,<sup>18</sup> however, concluded that the increase in entropy  $(S_2 - S_1)$  is a minimum and that  $(S_2 - S_1)/A$  is a maximum, where A is the available energy fed into the wave front. The variation of  $S_2$  along the  $\alpha$ , v curve may be evaluated at various densities within the accuracy of the equation of state employed by the equation

$$S_2 = S_2^0 + \bar{C}_v \ln T_2 / T_1 + nR \int_{v_0}^{v_2} dv / (v - \alpha), \quad (18)$$

where  $S_{2^0}$  is the entropy of the products of detonation in their standard state  $T_0$ ,  $v_0$ ,  $p_0$ . Actually Eq. (18) shows that there is a small change in  $S_2$  along the  $\alpha$ , v curve amounting to about 0.1 E.U./gram for a change in density  $(\rho_1)$  from 0.7 to 1.6 kg/L., the total entropy  $S_2$ being ~1.5 to 2.0 E.U./gram. Since  $\beta$  can be determined only to within about 5 percent (from measured velocities accurate to within 2 to 3 TABLE I. Constants of Eq. (19) for explosives shown in Fig. 1.

	D <sub>1.0</sub>	$M\left(\frac{\mathrm{m/sec.}}{\mathrm{kg}/1.0}\right)$	
PETN	5620	3500	
RDX	5900	3570	
TNT	4800	3500	
Tetrvl	5500	3350	
Picric acid	5060	3500	
Ammonium picrate	4800	3500	
Lead azide	$5100 \ (\rho_1 = 4.0)$	560	
Mercury fulminate	$5050 \ (\rho_1 = 4.0)$	890	

percent) it is evident that the slope of the  $\alpha$ , v curve gives  $(\partial \alpha / \partial v_2)_s$  with sufficient accuracy in the  $\alpha(v)$  approximation.

Figure 1 presents the  $\alpha$ ,  $v_2$  relations obtained by both methods (a) and (b). The data for the eight explosive compounds calculated by method (a) are best represented by the dotted curve. The solid curve was obtained entirely independently by method (b) for the same and a number of additional explosives, method (b) having preceded method (a) in the development of the theory. The deviations in  $v_2$  and  $\alpha$  from either the dotted or solid curve are about the same order of magnitude ( $\leq 3$  percent) as the experimental error involved in the measured detonation



<sup>18</sup> R. L. Scorah, J. Chem. Phys. 3, 425 (1935).

the present purposes, however, the form

$$x = KT^c/v \tag{21}$$

 $(d\alpha/dv_2)_S$  $\rho_2(kg/1.0)$  $v_2(1.0/kg)$  $\alpha(1.0/\text{kg})$ 0.8 1.25 0.75 0.30 0.39 0.68 1.0 1.00.837 1.2 0.62 0.47 1.4 0.714 0.56 0.53 0.625 0.51 0.59 1.6 1.8 0.555 0.47 0.65 2.0 0.50 0.43 0.69 0.455 0.39 0.73 2.2

velocities (assuming accurate heat data). The experimental velocity data used in these calculations are given by the following equation, the constants of which are given in Table I.

$$D = D_{1.0} + M(\rho_1 - 1.0), \tag{19}$$

where  $D_{1,0}$  is the velocity (m/sec.) at a density of 1.0 kg/L. and M is the slope of the  $D(\rho_1)$  curve in m/sec./kg/L.

#### CORRELATIONS

Not only do methods (a) and (b) give the same results within the limits of reproducibility of the data, but of even greater significance is the fact that all the explosives follow the same  $\alpha$  vs.  $v_2$ curve. This appears to be ample evidence that the last term in Eq. (9) is negligible. It is not, however, sufficient evidence that  $\bar{C}_{v} \cong \bar{C}_{v}^{*}$  (this approximation was made in both methods), although the validity of this assumption is strongly supported by the generality of the  $\alpha(v)$  function. In other words, RDX and PETN have detonation temperatures about 40 percent higher than ammonium picrate, picric acid, and TNT, showing that the dependence of  $\alpha(T, v)$  on temperature must be exceedingly small. The fact that values of  $\alpha$  for a given  $v_2$  for the latter explosives are consistently slightly higher than those of RDX and PETN at low density cannot be regarded as significant, since more recent velocity data indicate that in these cases values of  $D_{1,0}$  and M given in Table I are slightly in error in the direction giving low values of  $\alpha$ .

The equation of state employed by Kistiakowsky and Wilson<sup>8</sup> based on Bridgman's equation of state is very convenient for studying the magnitude of  $(\partial E/\partial v)_T$ . In the equation

$$pv = nRT(1 + xe^x). \tag{20}$$

Kistiakowsky and Wilson took  $x = K/T^{\frac{1}{2}}v$ . For

will be employed where K and c are constants, the latter of which will now be investigated. Equations (20) and (21) and the appropriate thermodynamic equation give

$$(\partial E/\partial v)_T = nRTxe^x(1+x)c/v, \quad (22)$$

$$\int_{\infty}^{v_2} (\partial E/\partial v)_T dv = -nRTxe^x c.$$
(23)

Comparing Eqs. (6) and (20), it is seen that  $xe^x = \alpha/(v-\alpha)$  and from Fig. 1 at  $v_2 = 0.5$  L./kg,  $(\partial E/\partial v)_T \approx 2.1 p_2 c$ . Thus the last term in Eq. (9) amounts to about 0.37c. Since methods (a) and (b) in which the last term in Eq. (9) is neglected give values of  $\beta$  agreeing within 5 percent (the dotted curve actually differs by less than 3 percent from the solid one), |c| cannot exceed 1/15. For c = -1/15, Eq. (23) gives an energy amounting to nearly 10 percent of  $Q + \Delta E$ . It is thus evident that  $\bar{C}_v \leq 1.1 \bar{C}_v^*$ . By comparing results obtained by methods (a) and (b) for a single explosive, e.g., PETN, using the same detonation velocity data, a more accurate comparison may be obtained by eliminating the effect of experimental error in D. Studies of this sort in fact indicate that the difference in  $\beta$  between the two methods is less than 3 percent and that, therefore,  $\bar{C}_v \leq 1.06\bar{C}_v^*$  at  $v_2 = 0.5$  L./kg. This result differs from that obtained by using Kistiakowsky and Wilson's value  $c = -\frac{1}{3}$ , which gives  $\bar{C}_{v} \approx 1.9 \bar{C}_{v}^{*}$ .

In connection with the approximation  $\alpha = \alpha(v)$ used in method (b) it is of interest to note that Bullen<sup>19</sup> recently introduced the hypothesis, based on his calculations of the earth's density distribution, that at pressures of the order of one million atmospheres the compressibility may be largely independent of chemical composition. The present investigation provides evidence that this may be at least approximately true even at much lower pressures, perhaps even as low as 25,000 atmos. (for temperatures above 2500°C).

It is interesting to compare the Eq. (6) with the following equation developed from statistical mechanics by Hirschfelder, Stevenson, and

<sup>&</sup>lt;sup>19</sup> K. Bullen, Nature 157, 405 (1946).

### EQUATION OF STATE AT HIGH PRESSURES

Eyring<sup>20</sup>

$$(p+a/v^2)v = nRT[1+b/v+0.625(b/v)^2 + 0.2869(b/v)^3 + 0.1928(b/v)^4].$$
(24)

At detonation pressures  $a/v^2$  may be neglected relative to  $p_2$  and Eqs. (6) and (24) then give

$$\alpha = v - v / [1 + b/v + 0.625(b/v)^{2} + 0.2869(b/v)^{3} + 0.1928(b/v)^{4}]. \quad (25)$$

If b is taken to be 0.95 L./kg (a reasonable value), Eq. (25) gives values of  $\alpha(v)$  agreeing with those of Fig. 1 within 5 percent at densities  $(\rho_2)$  up to 1.8 kg/L. Above 1.8 kg/L. it gives values of  $\alpha$ somewhat too large. Under the conditions encountered in detonation, Eq. (24) is equivalent to that proposed by Hirschfelder and Roseveare17 since the second virial coefficient B'(T) reduces approximately to b at high temperatures.

In reference (20) Happel's equation of state as

derived by Rameshchandra Majumdar,<sup>21</sup> namely

$$(p+a/v^2)v = nRT(1+b/v+5/6(b/v)^2 + 0.2869(b/v)^3 + \cdots), \quad (26)$$

was employed in arriving at Eq. (24). Actually Eq. (26) employing b=0.95 L./kg is in much better agreement with the curve of Fig. 1 than Eq. (24). In fact, it gives agreement within 0.03 L./kg in  $\alpha$  over the entire range shown. Even in the range of densities where Eq. (24) gives good agreement in  $\alpha$ , it does not give good agreement in  $(d\alpha/dv)$ . Equation (26) on the other hand gives good agreement in both  $\alpha$  and  $(d\alpha/dv)$ over the whole range of densities of interest in studies of the detonation of condensed explosives.

### CALCULATION OF DETONATION VELOCITY

Further rather convincing evidence for the generality of the curve of Fig. 1 is to be found in

-AE. It is	9.in 1	$^{\rho_1}$ kg/L.	D m/sec.	<sup>v</sup> 2 L./kg	α L./kg	e bill sv lo <b>ß</b> ille	n moles/kg	<i>T</i> ₂ ⁰K	W m/sec.	$p_2 \times 10^{-3}$ atmos.
PETN PETN PETN	BW	1.0 1.0	(5540)	0.725 (0.727)	0.546	0.65	35.2	5350 (4130)	1540 (1510)	85 (83)
PETN PETN PETN	BW R	1.2 1.2 1.2	(6210)	(0.620)	0.488	0.38	35.0	(3960)	(1600)	(117) (114)
PETN PETN PETN	BW	1.6 1.6 1.69	(7650)	$\begin{array}{c} 0.478 \\ (0.477) \\ 0.452 \end{array}$	0.405	0.49 0.46	34.9 34.9	5700 (3630) 5800	1820 (1800) 1900	225 (218) 255
PETN	LS	1.69	(8400)	(0.439)	0.545	0.64	40.5	5250	(2000)	(275)
RDX	BW	1.0 1.6 1.6	(5620)	(0.729) 0.469 (0.478)	0.394	0.48	40.5	(3980) 5750 (3570)	(1520) 2000 (1760)	(84) 255 (215)
TNT	DW	1.0	(1920)	0.740	0.570	0.65	33.1	(3370) 3700 (2170)	1250	(213) 60
TNT TNT TNT	LS	1.6 1.6 1.6	(4870)	(0.748) 0.505 (0.476)	0.447	0.48	24.5	(3170) 4170	(1250) 1340 (1680)	(00) 150 (190)
Tetryl	BW	1.6	(7290)	(0.496) 0.752	0.573	0.71	37.0	3170 4200	(1510) 1340	(175)
ciler of one-	BW	1.0 1.6 1.6	(5440) (7720)	(0.740) 0.485 (0.486)	0.415	0.50	35.5	(3620) 4700 3380	(1420) 1670 1710	(75) 200 209
	LS	1.63 1.63	(7600)	0.473 (0.465)	0.407	0.49	35.5	4750	1720 (1850)	210 (230)
Picric acid	BW	1.0 1.0	(5190)	0.746 (0.745)	0.572	0.68	36.2	3750 (3180)	1290 (1340)	65 (69)
6 2300°C).	BW	1.6 1.6 1.63	(7680)	(0.489 (0.492) 0.478	0.422	0.49	35.0	4150 (3080) (4200)	(1640) 1610	180 (199) 190
	LS	1.62	(7100)	(0.465)		Suit, prot		(envince) 20	(1730)	(210)

TABLE III. Detonation properties of various explosives.

\* Data given in ( ) are those computed by the investigators Brinkley and Wilson<sup>10</sup>-BW, Ratner<sup>7</sup>-R, and Landau and Stanyukovich<sup>4</sup>-LS.

<sup>20</sup> J. Hirschfelder, D. Stevenson, and H. Eyring, J. Chem. Phys. 5, 896 (1937).
<sup>21</sup> H. Happel, Ann. d. Physik 4, 21, 242 (1905); R. Majumdar, Bull. Calcutta Math. Soc. 21, 107 (1929).

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the fact that the (large diameter) velocities of detonation of explosives of widely different types have been calculated with an accuracy comparable to the experimental methods of velocity measurements by simply using the  $\alpha$  vs.  $v_2$  data taken from this curve. For example, velocities of various liquid and cast explosives have been calculated agreeing in all cases within 3 percent with measured velocities providing the measured detonation velocities were obtained in large enough diameter so that the maximum or hydrodynamic velocities were obtained. It is of interest to note that many explosives require charge diameters of the order of 5 in. before the maximum (complete reaction) velocity is reached. Whether or not the velocity is a maximum can usually be decided experimentally from velocity vs. charge diameter data at constant  $\rho_1$ . Table II lists data taken from the solid curve of Fig. 1 which may be used in the calculation of velocity.

### PROPERTIES OF EXPLOSIVES

Table III lists some detonation properties of several explosives calculated by method (a) using  $\bar{C}_v = \bar{C}_v^*$  and comparisons with results computed by other investigators. It will be observed that in general the agreement in compressibilities  $(v_1/v_2)$ , W and  $p_2$  is fairly good. The sharp differences in detonation temperature between BW (Brinkley and Wilson) and the present studies are to be expected as discussed previously (since BW used  $c = -\frac{1}{4}$  in Eq. (21)). Had BW adjusted the parameters of their equation of state to obtain better agreement between calculated and measured velocities in RDX, TNT, and picric acid the agreement between their studies and the present would have been even better (except for  $T_2$ ), since  $p_2 = \rho_1 D W \approx k \rho_1 D^2$ . It is possible that the calculations by BW have been improved in later studies. The data of LS for PETN at  $\rho_1 = 1.6$  are questionable, since they are inconsistent with the relation  $D/W = v_1/(v_1 - v_2)$ .

It is quite evident that the detonation temperature is really the only detonation property which may be used to provide experimental information on the accuracy of the various equations of state

employed in studies of the hydrodynamic theory of detonation, all other quantities being relatively insensitive to the form of the particular equation of state employed. The detonation temperature, however, is so sensitive to the form of the equation of state that a good method for measuring it should provide a crucial test of the validity of the equation of state. Fox,22 employing a special spectroscopic technique, measured the temperature from the side of the charge and his results for a number of military explosives correlated well with  $T_3 - T_1 = Q/\bar{C}_v^*$ . There is evidence from several types of experimental investigations that the conditions described as "detonation" conditions do not extend to the periphery of the charge, but that an "edge effect" exists. It is thus to be expected that the temperature at the edge of the charge adjacent to the detonation wave would correspond to the "adiabatic" temperature,  $(T_3)$ , rather than "detonation" temperature, T2. Cotter and Jacobs23 measured by similar spectroscopic means the temperature of liquid nitroglycerin both at the side and down the end of the charge and obtained temperatures of 4600°K and >5500°K, respectively. Calculations of the "adiabatic" and "detonation" temperatures by the methods outlined in the present report for nitroglycerin gave 4780°K for  $T_3$  and 5750°K for  $T_2$ , in good agreement with the measured values of Cotter and Jacobs. These measurements thus appear to provide evidence for the validity of the approximation  $\bar{C}_{v} \cong \bar{C}_{v}^{*}$  and the neglect of  $(\partial E/\partial v_{2})_{T}$ relative to  $p_2$  in Eq. (9) for  $\beta$ .<sup>24</sup>

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J. G. Fox, Navy Ordnance Report 200–45.
T. P. Cotter and S. J. Jacobs, OSRD Report 5618.

<sup>&</sup>lt;sup>24</sup> Since this article was prepared an interesting article by P. Caldirola [J. Chem. Phys. 14, 738 (1946)] has appeared treating by another procedure the subject of this study. Caldirola's method leads to temperatures and pressures which in some cases differ rather sharply from the results reported here. However, his definition of  $\sigma$  (in his Eq. 11) seems to be in error by a factor  $\frac{1}{2}$ . Moreover it may not in many cases be correct to neglect  $\frac{dA}{dv}$  as he has done. The results of the present study do not support the linear relations between  $\rho$  and  $1/\alpha$  claimed by Caldirola (his Eq. 13) although the discrepancies are not large.