# COMPRESSIBILITIES OF SOLIDS AND THE INFLUENCE OF INERT ADDITIVES ON DETONATION VELOCITY IN SOLID EXPLOSIVES

## BY MELVIN A. COOK University of Utah, Salt Lake City, U.S.A.

# Received 14th May, 1956

Experimental detonation velocity data are presented for 50/50 sodatol, 100/0, 95/5, 90/10, 85/15 and 80/20 RDX + water mixtures, 100/0 to 40/60 TNT + salt, 100/0 to 40/60 RDX + salt, 100/0 to 40/60 PDX + salt, 100/0 to 40/60 RDX + glass mixtures. The thermohydrodynamic theory is applied together with a theory of compressibility outlined in this article in computing the velocities of the explosive-inert mixtures. The results are compared with the observed velocities and shown to be in good agreement. The theoretical parameters of the compressibility equations are shown also to be in good agreement with the experimental data of Bridgman. Moreover, the computed total compressions compare favourably with data measured by Walsh and Christian up to 300-400 kilobars. Finally the  $\alpha(v)$  equation of state is examined for the above and some other mixtures and found to be of apparently general approximate validity. That is, the empirical curve discussed previously seems to apply within about 3 % in all of these mixtures.

The thermohydrodynamic theory provides, in solutions by the "inverse method", valuable empirical equation of state data. In this application one employs the observed velocity-density or  $D(\rho_1)$  data to solve for  $\alpha(T, v)$  in the equation of state

(1)



FIG. 1.-Correlation of explosives with " covolume " equation of state.

While it turns out that this method does not permit one to determine unambiguously the temperature dependent part of  $\alpha$ , results support the possibility that this component may be negligible and that  $\alpha(T, v) \cong \alpha(v)$ . Perhaps the most striking

203

#### COMPRESSIBILITIES OF SOLIDS

support of this approximation is to be found in the apparently general  $\alpha(v)$  relation applicable in detonation illustrated in fig. 1.1 Even more substantial evidence has recently been found in the influence of density on the rate of chemical reaction for TNT, ammonium nitrate and sodium nitrate.<sup>2, 3, 4</sup> One finds that the reaction rate increases with density at a rate corresponding to a temperature increase with density of about 500-1000° K cm<sup>3</sup> g<sup>-1</sup>. Since one may show that the increase in rate is almost entirely a normal temperature effect and not a pressure one, this result may be seen to support the  $\alpha(v)$  approximation 2, 5, 6, 7 since this is approximately the density coefficient of temperature required by this approximation. Moreover, the most recent direct temperature measurements support this conclusion.8

In this article the validity of the  $\alpha(v)$  curve of fig. 1 is examined for explosives containing sodium nitrate, water and various inert additives. A general theory of thermal expansion and compressibility of solids is then presented based on elementary fundamental considerations. This theory is then applied in computing the detonation velocities of explosives with inert additives ranging from zero to 60% or more inert, and in further study of the covolume equation of state and the general  $\alpha(v)$  curve.

## EXPERIMENTAL

The measured velocities summarized in table 1 were obtained by either the "pinoscillograph" or "streak" camera method. Both of these methods have good reproducibility, but it is not always possible to control density as accurately, and the experimental error is therefore largely that associated with density fluctuations amounting to as much as about 3 % in loose-packed charges. Besides those examples of explosives containing sodium nitrate (SN) in fig. 1, SN was studied in 50/50 TNT + SN (cast and

TABLE 1.—EXPERIMENTAL DETONATION VELOCITY DATA (msec<sup>-1</sup>)

 $D_{1} = 1 S(z_{1} - 1, 0)$ 

D -

	23. 3	$\mathbf{p} = \mathbf{p}_{1:0} + \mathbf{p}_{0}$	10)		
	mixture	D <sub>1.0</sub>	S	ran measu	ge of rements
	50/50 TNT + sodium nitrate	5100	2580	1.0-1.85	g cm <sup>−3</sup>
	100/0 RDX + water	5900	3650	0.8-1.7	.,,
	95/5 RDX + water	5900	3650	0.9-1.4	,,
	90/10 RDX + water	5900	3650	0.9-1.4	**
	85/15 RDX + water	5700	3650	0.9-1.4	,,
	80/20 RDX + water	5580	3650	1.2-1.3	
	100/0 pentolite (50/50) + salt				
	(-20 + 28  mesh)	5480	3100	0.6-1.65	,,,
	70/30	4590	3200	1.4-1.85	,,
	40/60	3000	3500	1.35-1.7	,,
	54/46	6780			
	B. $D = D$	$p_{\rho_1}(1.0) - S'x; \ (x =$	$=1-N_w$		
		ρ1	$D_{\rho_1}(1.0)$	S'	range of measureme
N	$\Gamma$ + salt	1.5	6640	3100	0-60 %
f(x)	) = 0)	1.35	6145	3185	0-60 ,,
		1.2	5655	3380	0-60 ,,
		1.0	5010	3530	-0-60 ,,
N	$\Gamma + \text{glass}$		1000		
(t	peads $-20 + 28$ mesh) [ $\rho_1 = 0^{-1}$	82 + 0.87x]	4650	2170	0-60 "
(-	$X + salt - 20 + 28 mesh)$ [ $\rho_1 = 1$ ·	$22 + 0.3(x + x^2)$ ]	6765	2775	0-60 ,,
.D. (b	X + glass eads $-20 + 28$ mesh) [ $\rho_1 = 1$ .	$20 + 0.4x + 0.8x^2$ ]	6630	2550	0-60 "

Its

204

F R

#### M. A. COOK

loose-packed mixtures). The ideal or hydrodynamic velocities were measured in 20-25 cm diameter charges using -48 mesh and ball-milled SN. RDX + water mixtures were also studied to determine the influence of added water on the  $\alpha(v)$  curve.  $D(\rho_1)$  data for these mixtures were obtained for 100/0, 95/5, 90/10, 85/15 and 80/20 mixtures, but  $\alpha(v)$ calculations were made only for the 100-0 and 90-10 mixtures. Pressed and hand-packed charges were used depending on the density desired. For the 90/10 mixture five shots were measured at each of the end points of the  $D(\rho_1)$  curve ( $\rho_1 = 1.4 \pm 0.05$  and  $0.9 \pm 0.05 \text{ g cm}^{-3}$ ). Between these densities measurements were made in duplicate at  $0.1 \text{ g cm}^{-3}$  intervals. Densities were determined by total weight/total volume measurements. For inert additives, salt and glass beads of -20 + 28 mesh particle size were used in TNT, RDX and 50/50 pentolite; and TNT and RDX, respectively. One must select particle sizes carefully if an additive is to behave strictly as an inert. For example, one may show that very fine (e.g. ball-milled) salt vaporizes in the detonation wave and quenches detonation if used to the extent of more than about 10 % even in the most sensitive explosives. On the other hand, if it is too coarse, detonation may propagate at or near the velocity of the pure explosive, by propagation between inert grains. It is believed that the -20 + 48 mesh size approximately satisfies the requirements for an inert additive at least for the inert substances considered here. The velocity D obtained from the smoothed curves of the experimental data are summarized in table 1 by means of the following two empirical formulae.

$$D = D_{1.0} + S(\rho_1 - 1.0), \tag{2}$$

$$D = D_{\rho_1}(1.0) - S'x; \ \rho_1 = \rho_1(1.0) + f(x), \tag{3}$$

where  $D_{1.0}$ , S,  $D_{\rho_1}$  and S' are constants,  $x = 1 - N_{\mu}$  = fraction of inert present and f(x) is a variable defined in table 1.

#### HYDRODYNAMIC EQUATIONS

Using the covolume equation of state in conjunction with the hydrodynamic theory the ideal detonation velocity is given by

$$D^* = v_1(v_1 - \alpha^*)^{-1} \left(\beta^* + 1\right)\beta^{*-\frac{1}{2}} \left(n^* R T_2^*\right)^{\frac{1}{2}},\tag{4}$$

#### where

$$\beta^* = (C_{\nu}^* + n^* R) / C_{\nu}^* - (\mathrm{d}\alpha^* / \mathrm{d}v_2^*)_S.$$
<sup>(5)</sup>

Here the star refers to the pure explosive and the corresponding unstarred equation to the explosive + inert mixture. If a pure explosive and one containing an inert additive are compared for the same free space, one may take  $\beta = \beta^*$ , especially since the term  $(\beta^* + 1)/\beta^{*\frac{1}{2}}$  is very insensitive to variations in  $\beta^*$  for the usual range of this variable. Comparing (4) for a pure explosive with the corresponding unstarred equation for the explosive + inert mixture one thus obtains

$$D/D^* = A(nT_2)^{\frac{1}{2}}/A^*(n^*T_2^*)^{\frac{1}{2}},$$
(6)

where  $A = 1/(1 - \rho_1 \alpha)$  and  $A^* = 1/(1 - \rho_1 \alpha^*)$ . Making use of the covolume equation of state ( $\alpha = \alpha(v)$ ) one may express the detonation temperatures for the two cases as follows:

$$T_2^* = (Q^* - C_v^* T_1) / (\overline{C}_v^* - n^* R/2\beta^*); \ T_2 = (Q - \overline{C}_v T_1) / (\overline{C}_v - n R/2\beta).$$
(7)

Since for a strictly inert mixture,  $C_v = N_w C_v^*$ ,  $Q = N_w Q^*$  and  $n = Nn^*$  for  $\beta = \beta^*$  one may equate  $T_2^*$  to  $T_2$  and obtain

$$D/D^* = (A/A^*)N_{\psi^{\frac{1}{2}}}.$$
(8)

Likewise, since

$$p_2^* = \rho_1 D^* (n^* R T_2)^{\frac{1}{2}} / \beta^{\frac{1}{2}}, \tag{9}$$

one may write

$$p_2/p_2^* = \rho_1 D N_w^{\frac{1}{2}} / \rho_1 D^*.$$
(10)

The covolume of the explosive + inert mixture upon which A depends may be taken as the sum of the covolumes of the detonation products and the volume of the inert. Thus

P

$$\alpha = \alpha_{\rm E} + \alpha_{\rm I} = N_w \alpha^*(p) + V_{\rm I}(p), \tag{11}$$

where  $\alpha^*$  applies to the pure explosive and  $\alpha_I(p) = V_I(p)$  is pressure dependent through the appropriate compressibilities. The former may be found from a plot of  $p_2$  against  $\alpha^*$ 

#### COMPRESSIBILITIES OF SOLIDS

for the pure explosive. Since the covolume of the products of detonation for the pure, ideal explosive obeys the same  $\alpha(v)$  curve, the covolume  $\alpha$  may itself be relatively insensitive to composition and temperature. Consequently, the  $\alpha^*(p)$  plot desired for the solution of the explosive-inert problem is simply the  $\alpha^*(p^*)$  plot for the pure explosive, and  $\alpha_E = N_w \alpha^*(p)$  corresponding to the pressure  $p_2$  of the mixture, obtained by use of the observed ratio  $\rho_1 D/D^* \rho_1^*$  for the explosive + inert system. Typical  $\alpha^*(p)$  plots are shown for TNT in fig. 2.



FIG. 2.—Covolume-pressure relationship for TNT.

The covolume  $\alpha_I$  of the inert is simply the volume occupied by the mass of inert at the pressure in question and is given by

$$\alpha_{\rm I} = V_{\rm I}(p) = V_{\rm I_0} \exp\left(-\int_0^p \beta dp\right). \tag{12}$$

The procedure in solving this problem is as follows. Assume a value of  $D/D^*$ , and compute  $p/p^*$  from eqn. (10). One may then compute  $\alpha_I$  and obtain  $\alpha$  from this result and  $\alpha_E = N_w \alpha^*(p)$ , where  $\alpha^*(p)$  is taken from plots such as those in fig. 2. Then from eqn. (8) one may compute  $D/D^*$  through the definitions of A and  $A^*$ . If the  $D/D^*$  ratio does not agree with the assumed one, the solution is repeated with the new value, and so on until a self-consistent solution is obtained.

#### THEORY OF $\alpha_I$

The heat content of a solid may be related to the total expansion  $\Delta R/R$  as follows:

$$H = \int_0^T C dT = \int_{R_0}^R \frac{\partial E}{\partial R} dR = R_0 \frac{\partial E}{\partial R} \frac{R - R_0}{R_0}.$$
 (13)

From the virial theorem,  $2\overline{T} = \overline{R_0 \partial E/\partial R}$ , where  $\overline{T}$  is here the average kinetic energy and one may thus write (13) in the form  $H/2\overline{T} = (R - R_0)/R_0$  for small expansions. From this result one obtains for the linear expansion coefficient  $\alpha' = C/2\overline{T}$ , where C is heat capacity.

Now for T, following arguments discussed previously,<sup>9</sup> one may make use of the semiempirical relations

$$\overline{T} \simeq \epsilon_0' \simeq \phi + \epsilon_c \simeq 2\epsilon_c, \tag{14}$$

where  $\phi$  is the work potential,  $\epsilon_0'$  the band width and  $\epsilon_c$  the cohesive energy. These relations, while justifiable on a purely empirical basis, were first suggested by the concept of the author's "non-coulombic constraint virial" <sup>10</sup> which appears to permit one to attribute bands in solids simply to line broadening by vibrational states. One may easily show <sup>11</sup> that  $\epsilon_0' = \Delta T_{\text{max}}$ , where  $\Delta T_{\text{max}}$  is the kinetic energy fluctuation of a bond due to the normal vibrations. This fluctuation in *T* is shown to be twice the "non-coulombic constraint virial" which in turn is equal to the bond energy. The implication is that chemical bonding is to be associated exclusively with this "constraint virial".<sup>9-11</sup> The linear expansion coefficient of an isotropic solid should then be

$$\alpha' \cong C/2(\phi + 1/2\epsilon_0') \cong C/2(\phi + \epsilon_c) \cong (8\pi)^{\frac{5}{3}} Cm/(3\rho)^{\frac{5}{3}}h^2.$$
(15)

### 206

#### M. A. COOK

This treatment considers only ideal perfect crystals, and ignores expansion associated with thermodynamic defects such as the Schottky or Frenkel types.<sup>12</sup> However, one may show that these should become important only at temperatures approaching the melting point as far as  $\alpha'$  and  $\Delta R/R_0$  are concerned. The validity of eqn. (15) is illustrated in table 2.

metal	Т (°К)	φ	ε0'	280	α	α' (× 106)* (calc.)†		
aidio a		(eV)	(eV)	(eV)	(1)	(2)	(3)	(× 106)
Cu	50 100 208	4.43	7.04	7.1	4·1 10·8	4·2 11·1		4·1 10·1
Ag	100 200 298	4.3	5.51	5-9	14·5 17·1 17·7	13·9 16·4 17·0	22.6	14·1 18·1 19·0
Au	100 200 298	5.17	5.54	7.2	14·4 15·9 16·3	12·7 14·0 14·4	23.4	11.8 13.7 14.2
Li	298	2.39	4.6	3.4	25.5	29.3	26	56
Na	298	2.26	3.2	2.26	37.6	42.9	45	71
K	298	2.13	2.14	1.74	48.0	49.5	71	83
Mg	298	3.48		3.12		24.7		26
Ca	298	2.74		4.18		27.1		22
Zn	298	3.74		2.34	· (3107	27.2		39.7
Cd	298	3.91		2.34		26.9		29.8
Al	298	3.74		4.78		20.5		25.5
Sn	298	4.74		6.78		17.1		23
Pb	298	4.64		4.14		27.8		29.3
Fe	175 225 273 298 373 573	4.35		8.18		12·8 14·0 14·8 14·9 16·7 20·2		9·1 10·5 11·5 11·7 12·7 15·0
Ni	298	4.78		7.40		15.3		13.3

TABLE	2.—LINEAR	EXPANSION	COEFFICIENT	OF	METALS *
-------	-----------	-----------	-------------	----	----------

\* work potential  $\phi$  from Michealson;<sup>13</sup>  $\epsilon_0$ ' from Sommerfield equation:  $\epsilon_0' = \frac{\hbar^2}{2m} \left(\frac{3\rho}{8\pi}\right)^{\frac{3}{3}}$ ; cohesive energy  $\epsilon_c$  from Mott and Jones <sup>14</sup> and Seitz,<sup>15</sup> observed  $\alpha'$  data are from *Metals Handbook* (1950) and Dorsey.<sup>16</sup>

 $\dagger (1) \ \alpha' = C/2(\phi + 1/2\epsilon_0'); \ (2) \ \text{from} \ \alpha' = C/2(\phi + \epsilon_c); \ (3) \ \text{from} \ \alpha' = C/\frac{\hbar^2}{m} \left(\frac{3\rho}{8\pi}\right)^{\frac{3}{2}}.$ 

The same fundamental principles are applicable in describing quantitatively the compressibility  $\beta = (\partial V/\partial p)/V$ . As in thermal expansion the "orbital volume" may be related reciprocally to the kinetic energy  $\overline{T}$ , and the compression to the change in kinetic energy in the orbital due to the applied pressure. If  $\Delta \overline{T}$  is the increase in  $\overline{T}$  per mole due to an applied pressure, one may write  $\Delta \overline{T} = -\frac{3}{2}RFN$  where F is the total force (negative for compression) applied to an atom, in the metal along each of the three principal axes, N is Avogadro's number, and R the average diameter of the atom. The relative compression is determined by that of the valence orbital shell of the atom. Since the core or inner electron will also take up some of the force and total  $\Delta T$ , one must evaluate that part  $F_1$  and  $\Delta T_1$  of the total F and  $\Delta T$  that goes only into the outermost, or size-determining orbital. Thus,  $F = \sum_{i=1}^{z} F_i$ , where  $F_i$  is the effective force applied on each of the z electron orbitals by the total force F. Hence using  $\Delta T_1$  in place of H in

#### COMPRESSIBILITIES OF SOLIDS

eqn. (13) one obtains for the linear compression :  $\Delta R/R = -\Delta T_1/2T = 3RF_1N/4\overline{T}$  giving  $\beta = -9RM^{\frac{3}{2}N^{\frac{1}{2}}/4\rho_1^{\frac{3}{2}}\overline{T}\phi}$ , where *M* is the atomic weight,  $\rho_1$  the density and  $\phi = 1 + \sum_{j=1}^{z} F_j/F_1$ .

Since

$$F = \phi F_1 = p/n_0^{\frac{3}{2}} = p(M/N\rho_1)^{\frac{3}{2}}$$

one therefore obtains

$$\beta = 2 \times 10^{-6} RM^{\frac{6}{5}}/T\phi \rho_1^{\frac{6}{5}}.$$

(16)

for R in Å, T in eV and  $\rho_1$  in g cm<sup>-3</sup>.

To estimate  $\phi$  it is here assumed that  $F_i \propto \bar{r}_i^2$ , where  $\bar{r}_i$  is the effective average orbital radius of the *i*th electron. Then from the Fermi-Thomas model one obtains  $F_i/F_k = E_k/E_i$ ,

and  $\phi = 1 + \sum_{i=2}^{\infty} E_i E_i$ , where  $E_i$  is the electronic energy level of the *i* th electron. Since

each orbital in a closed shell contains two electrons of opposite spin one may evaluate  $E_1/E_i$  with sufficient accuracy by building up the core in pairs assuming perfect screening by inner filled orbitals. The only difficulty comes in knowing  $E_i$  for i < about 6. Fortunately one may frequently determine these from measured ionization potentials taking into account the valence structure of the atom. It is, of course, important to know whether valence electrons are coupled as in helium (two electron bonds) or are uncoupled in effectively single electron bonds as in metals. The  $\phi$ s are sufficiently sensitive to the type of coupling that one should have little difficulty in deciding the valence structure from the observed  $\beta_0$  (the low pressure value of  $\beta$ ). This is justified from the excellent agreement in cases where there is no uncertainty in this factor, e.g., lithium and sodium. One finds, for example, that the outer three electrons of aluminium should be treated as a one-electron bond with two underlying coupled electrons, rather than to assume that all three valence electrons have equal energy.

Our interest here concerns  $\beta$  at very large pressures. This may be obtained from the value at atmospheric pressure  $\beta_0$  and the variations of R,  $\overline{T}$  and  $\phi$  with pressure by the application of eqn. (16). If one assumes that only  $E_1$  is influenced significantly when pressure is applied, one finds that

$$\beta = \beta_0 + \int_0^p \frac{\partial \beta}{\partial p} dp = \beta_0 + \int_0^p \beta \left\{ \frac{1}{V} \frac{\partial V}{\partial p} - \frac{1}{\overline{T}} \frac{\partial T}{\partial p} - \frac{1}{\overline{\phi}} \frac{\partial \phi}{\partial p} \right\} dp$$
$$= \beta_0 + \int_0^p \beta \left\{ \frac{1}{V} \frac{\partial V}{\partial p} + \frac{2}{3V} \frac{\partial V}{\partial p} + \frac{2}{3V} \frac{\partial V}{\partial p} \left( 1 - \frac{1}{\phi_0} \right) \right\} dp = \beta_0 - \int_0^p a\beta^2 dp.$$

Hence, taking  $a = 2.33 - 0.67 \phi_0^{-1}$ , one obtains

$$\beta = \beta_0 \sum_{i=0}^{\infty} (-a\beta_0 p)^i.$$
(17)

Mott and Jones showed that the  $\beta(T)$  relation is  $\frac{1}{\beta} \frac{\partial \beta}{\partial T} = \frac{\alpha}{\gamma} V^2 \frac{d^2 \ln \nu}{dV^2}$ , where  $\alpha$  is the

volume expansion coefficient, and  $\gamma = \alpha V_0 \beta_0^{-1} C^{-1} = - d \ln \nu/d \ln V$ ,  $\nu$  being the characteristic frequency and C the heat capacity. Hence, applying the above theory one obtains the very simple relation

 $d \ln \beta / dT = a\alpha = 3a\alpha'. \tag{18}$ 

Bridgman's results are expressed by the equation  $\beta = a' \times 10^{-7} - 2b \times 10^{-12}p$  and apply up to about 50 to 100 kilobars. Hence one expects to find  $\beta_0 = a' \times 10^{-7}$  and  $a\beta_0^2 = ab \times 10^{-12}$ . Table 3A evaluates this comparison and shows that the theoretical values of  $\beta_0$  are in remarkable agreement but that the ratio  $2b \times 10^{-12}/a\beta_0^2$  (theoretically unity) ranged from 1.0 for strontium to 12.6 for platinum. This indicates that the semiempirical method used here for handling the pressure coefficient of  $\beta$  while not exact is correct as to order of magnitude. Table 3B compares results of  $V/V_0$  (total compression) at 200-400 kilobars measured by Walsh and Christian <sup>18</sup> with results computed from the equation

$$V/V_0 = \exp\left[+\sum_{i=1}^{\infty} (-a\beta_0 p)^{i/ai}\right].$$
(19)

## 208

#### M. A. COOK

obtained by integration of eqn. (17). The agreement is somewhat better than one might expect from the ratio  $2b \times 10^{-12}/a\beta_0^2$  found in the comparison with Bridgman's data. The theoretical temperature coefficient from eqn. (18) is compared in table 3C with results discussed by Mott and Jones.<sup>14</sup> Again order-of-magnitude agreement is obtained. While only in approximate agreement all of these results should be considered in the light of the simplicity and approximate nature of the theory.

TABLE 3.-COMPARISONS OF THEORETICAL AND OBSERVED COMPRESSIBILITIES

#### A. WITH BRIDGMAN 17

solid	φ <sub>0</sub>	$a'  imes 10^{-7}/eta_0$	$2b \times 10^{-12}/a\beta_0^2$
copper	3.5	0.92	3.7
silver	4.4	1.07	4.9
lithium	1.14	1.008	1.5
sodium	1.51	1.08	1.5
beryllium	2.15	0.85	3.2
magnesium	2.13	0.96	2.0
calcium	2.2	0.98	1.4
strontium		(1.0)	1.0
barium	· - ·	(1.0)	1.14
aluminium	2.10	0.96	2.5
silicon	4.75	0.84	
iron	0 10 10-10	(1.0)	5.6
platinum		(1.0)	12.6
diamond	2.92	1.0	

#### B. WITH WALSH AND CHRISTIAN 18

	P/Po							
P	$= 10^5$ atm	$10^5 \text{ atm} \qquad p = 2 \times 10^5 \text{ atm}$		$p = 3 \times 10^5$ atm		$p = 4 \times 10^5$		
	(calc.)	(calc.)	(obs.)	(calc.)	(obs.)	(calc.)	(obs.)	
aluminium	0.888	0.807	0.843	0.748	0.796	*	0.759	
copper	0.930	0.875	0.893	0.831	0.866	0.791	0.838	

\* theoretical series nonconvergent at  $p \ge 3.3 \times 10^5$  atm.

#### C. $10^3 d \log \beta / dT$

	(1) (calc.)	(2)	(obs.) 14
lithium	0.40	0.77	0.71
sodium	0.62	1.03	1.20
calcium	0.41	0.33	0.60
aluminium	0.31	0.38	0.55
lead	0.42	0.44	0.56
(1) from $\alpha$ :	$= 3C/2(\phi + \epsilon_c);$	(2) from	observed a.

Finally, detonation velocities of several explosives with inert additives were computed by the method outlined above using this theory of compressibility. The results are summarized in table 4, together with the data taken from the smoothed experimental data. In general, the calculated and observed data are seen to be in good agreement over the entire range of compositions. This, however, is a much less critical evaluation of the theory of compressibility than, for example, the comparisons with the data of Walsh and Christian because either  $\alpha_{I}/\alpha$  was relatively low (large  $N_{w}$ ), or the pressure was so low (small  $N_{w}$ ) that  $\alpha_{I} \sim \alpha I_{0}$ .

The important application of the thermohydrodynamic theory to this problem concerns the  $\alpha(v)$  curve. In fig. 3 are plotted the calculated  $\alpha(v)$  data for these explosives. Included also are the  $\alpha(v)$  data computed by the "inverse method" for 50-50 TNT + SN and 90-10 RDX + water. The results seem to support the approximate generality of the empirical  $\alpha(v)$  curve and the equation of state (1).



FIG. 3.—Covolume relations in explosives with inert additives.

TABLE 4.—COMPUTED VELOCITIES FOR EXPLOSIVE + INERT MIXTURES

A. 1	D =	$D_{1.0}$	+ 2	$(\rho_1 -$	1.0)

			$D_{1.0}$ (m sec <sup>-1</sup> )			$S \text{ (m sec}^{-1} \text{ g}^{-1} \text{ cm}^3)$	
	explosive		(calc.)	(obs.) (interpolate		(calc.)	(obs.)* (interpolated)
100/0	TNT + salt'	0.866	(5010)	5010		(3225)	3225
90/10	TNT + salt		4710	4660		3265	3340
80/20	TNT + salt		4405	4305		3330	3410
70/30	TNT + salt		4050	3950		3435	3220
60/40	TNT + salt		3610	3600		3610	3560
50/60	TNT + salt		3070	3245		3840	3650
40/60	TNT + salt		2415	2980		4145	3740
100/0	50/50 pentol	ite + salt	(5480)	5480		(3100)	3100
80/20	50/50 pentol	ite + salt	4900			3120 .	
70/30	50/50 pentol	ite + salt	4600	4590		3190	3200
54/46	50/50 pentol	ite + salt	3885	6780 (1.8	5)	3420	
40/60	50/50 pentol	ite + salt	3070	3000		3735	3500
100/0	RDX + salt		(5900)	5900		(3570)	3570
70/30	RDX + salt		4935			3095	
40/20	RDX + salt		3300			3535	
20/80	RDX + salt		1730			4180	
DX + s	alt p1	D (calc.)	D (obs.)	TNT + glass	ρ1	D (calc.)	D (obs.)
70/30	1.33	5930	5825	80/20	1.0	4260	4200
40/60	1.51	5150	5100	40/60	1.34	3190	3350
LDX + g	lass*			TNT +	copper	per $D$ (calc.) = 6900 - 2760	
80/20	1.34	6165	6150	$(\rho_1 =$	1.59 +	$1 \cdot 3x + x^2 +$	- 2x <sup>3</sup> )
60/40	1.48	5520	5590	TNT +	PbSO	D (calc) =	= 6900 - 2480 -
40/60	1.76	4990	5100	(01	= 1.59	$+ x + 1.6x^{-1}$	2)
* 0	for these exc	man dans l	1.0 10-7		10-6	DECO	04 10-6

\*  $\beta_0$  data used: copper:  $7.8 \times 10^{-7}$ ; salt:  $4.18 \times 10^{-6}$ ; PbSO<sub>4</sub>:  $1.94 \times 10^{-6}$ : glass: ( $\alpha_I = \alpha_{I_0}$ ).

+ agreed within  $\pm$  200 m/sec from  $N_w = 1.0$  to 0.27 (data in classified literature).

The  $\alpha(v)$  curve *per se* provides a means of estimating the validity of the  $\alpha(v)$  approximation. In the limit of low pressures,  $\alpha$  should emerge smoothly into the van der Waals *b*. Hence, as a covolume,  $\alpha$  should be about four times greater than the actual volume  $v_m$  of the molecules. Hence one should have for the internal energy increase due to the applied pressure *p*,

$$E_i = -\frac{1}{4} \int_0^p p d\alpha \cong -\frac{nRT}{4} \int_0^v d\alpha/(v-\alpha).$$

The integral has as an upper limit for CHNO explosives a value of about 2.5 giving an upper limit value for  $E_i$  of about 200 cal/g. But Q (the heat of explosion) plus the Hugoniot energy  $\frac{1}{2}p(v_1 - v_2)$  is in this upper limit case about 1800 cal  $g^{-1}$  giving  $E_i/(Q + \frac{1}{2}p(v_1 - v) = 0.1$  to 0.15.

One may also estimate  $E_i$  directly by the methods used here for thermal expansion and compressibility of solids. Thus

$$E_i = \Delta T = \int_0^p p dv = \int_0^p v_m p \left(\frac{1}{v_m} \frac{dv_m}{dp}\right) dp < v_m \beta p^2/2.$$

The theory for molecules of the type considered here also gives  $\beta_0 \leq 10^{-6}$  atm<sup>-1</sup>. Since  $\bar{v}_m$  should have an upper limit of 0.5 cm<sup>3</sup> g<sup>-1</sup>, one thus obtains  $E_i \sim 200$  cal g<sup>-1</sup> in agreement with the above estimate.

According to these estimates therefore, while the  $\alpha(v)$  equation of state gives an upper limit for  $T_2$ , the actual value should be no more than 10-15 % (or about 500° K) less. This is, however, in sharp contrast with the approximately 3000° K lower values for  $T_2$ computed for PETN at  $\rho_1 = 1.7$  g cm<sup>-1</sup> by Cottrell and Paterson.<sup>19</sup>

The author wishes to acknowledge the assistance of members of "Explosives Research Group" University of Utah, in the velocity measurements and some of the calculated data presented in this article. Special mention is due Mr. Donald W. Robinson, now at Case Institute, Ohio, Wayne O. Ursenbach, assistant director, ERG, and Carl D. Spear, graduate student. This investigation was supported in part by the Office of Naval Research.

- <sup>1</sup> Cook, J. Chem. Physics, 1947, **15**, 518; 1948, **16**, 554, 1165; see also Paterson, J. Chem. Physics, 1948, **16**, 159, 847.
- <sup>2</sup> Cook, Keyes, Horsley and Filler, J. Physic. Chem., 1954, 58, 1114.
- <sup>3</sup> Cook, Horsley, Partridge and Ursenbach, J. Chem. Physics, 1956, 24, 60.
- <sup>4</sup> Cook and Ursenbach, 2nd ONR Symp. Detonation (Feb. 9-11, 1955, Washington, D.C.), p. 401.
- <sup>5</sup> Paterson, Research, 1948, 1, 221.
- <sup>6</sup> Murgai, J. Chem. Physics, 1956, 24, 635.
- 7 Caldirola, J. Chem. Physics, 1946, 14, 730.
- <sup>8</sup> Gibson, Bowser, Summers, Scott, Cooper and Mason, 2nd ONR Symp. Detonation (Feb. 9-11, 1955, Washington, D.C.), p. 50.
- 9 Cook, Bull. no. 53, 42, no. 2, 1951, Utah Eng. Expt. Station.
- <sup>10</sup> Cook, J. Chem. Physics, 1945, 13, 262; 1946, 14, 62; J. Physic. Chem., 1947, 51, 407; Utah Acad. Sci., Arts Letters, 1948, 25, 145.
- 11 Cook, Bull. no. 74, 46, no. 16, Nov. 30, 1955 (Utah Eng. Expt. Station).
- <sup>12</sup> Mott and Gurney, *Electronic Processes in Ionic Crystals* (Oxford, Clarendon Press, 1953).

13 Michealson, J. Appl. Physics, 1936, 21, 536.

- 14 Mott and Jones, Properties of Metals and Alloys (Oxford, Clarendon Press, 1936).
- 15 Seitz, Modern Theory of Solids (McGraw Hill Co., 1940).
- 16 Dorsey, Physic. Rev., 1907, 25, 88.
- 17 Bridgman, The Physics of High Pressures (MacMillan Co., New York, 1951).
- 18 Walsh and Christian, Physic. Rev., 1955, 97, 1544.
- 19 Cottrell and Patterson, Proc. Roy. Soc. A, 1952, 213, 214.