

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 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.

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

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

where $D_{1.0}$, S , D_{ρ_1} and S' are constants, $x = 1 - N_w =$ 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

$$D^* = v_1(v_1 - \alpha^*)^{-1}(\beta^* + 1)\beta^{*-1/2}(n^*RT_2^*)^{1/2}, \quad (4)$$

where $\beta^* = (C_v^* + n^*R)/C_v^* - (d\alpha^*/dv_2^*)_S$. (5)

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 $(\beta^* + 1)/\beta^{*1/2}$ is very insensitive to variations in β^* 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

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

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:

$$T_2^* = (Q^* - C_v^*T_1)/(\bar{C}_v^* - n^*R/2\beta^*); \quad T_2 = (Q - \bar{C}_vT_1)/(\bar{C}_v - nR/2\beta). \quad (7)$$

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

$$D/D^* = (A/A^*)N_w^{1/2}. \quad (8)$$

Likewise, since

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

one may write

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

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

$$\alpha = \alpha_E + \alpha_I = N_w \alpha^*(p) + V_I(p), \quad (11)$$

where α^* 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 α^*

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 α 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 $p_1 D/D^* p_1^*$ for the explosive + inert system. Typical $\alpha^*(p)$ plots are shown for TNT in fig. 2.

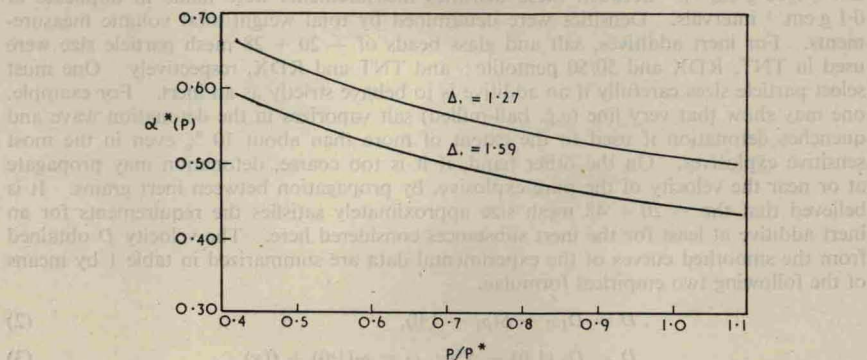


FIG. 2.—Covolume-pressure relationship for TNT.

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

$$\alpha_I = V_I(p) = V_{I0} \exp \left(- \int_0^p \beta dp \right). \quad (12)$$

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 α_I and obtain α 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 α_I

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

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

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

Now for \bar{T} , following arguments discussed previously,⁹ one may make use of the semi-empirical relations

$$\bar{T} \cong \epsilon_0' \cong \phi + \epsilon_c \cong 2\epsilon_c, \quad (14)$$

where ϕ is the work potential, ϵ_0' the band width and ϵ_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"¹⁰ which appears to permit one to attribute bands in solids simply to line broadening by vibrational states. One may easily show¹¹ that $\epsilon_0' = \Delta T_{\max}$, where ΔT_{\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".⁹⁻¹¹ The linear expansion coefficient of an isotropic solid should then be

$$\alpha' \cong C/2(\phi + 1/2\epsilon_0') \cong C/2(\phi + \epsilon_c) \cong (8\pi)^{1/3} C m / (3\rho)^{1/3} \hbar^2. \quad (15)$$