from Eq. (13) is quite insensitive to different values of β and nT_2 .

For evaluating the products of detonation a modification of the method developed by Brown¹⁴ was employed together with heat data taken from Bichowski and Rossini,¹⁵ and Schmidt.¹⁶ 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 Roseveare¹⁷ showed that for gases at sufficiently high temperature the internal energy is a linear function of density (ρ) . 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 ρ 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 β .) Hirschfelder and Roseveare showed that the linear variation of E with ρ 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 β , the last term in (9) being neglected following the reasoning already given. As a first approximation α 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 β . A plot of α 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 β obtained by including the term from the first approximation are introduced back into Eq. (13) to obtain better values of α , the quantity nT_2 also being corrected according to its dependence on β , v_2 , and α . This process is repeated until all parameters converge to constant values. As in method (a) this series of approximations also converges rapidly.

In evaluating β by means of the slope of the

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

¹⁵ F. R. Bichowski and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Company, New York, 1936).

¹⁶ Á. Schmidt, Zeits. f. das gesamte Schiess u. Sprengstoffwesen 29, 259 (1934).

¹⁷ J. O. Hirschfelder and W. E. Roseveare, J. Phys. Chem. **43**, 15 (1939).

 α , v curve it was tacitly assumed that the entropy S_2 is constant along the curve. At any density (ρ_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,¹⁸ 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 α , 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 α , v curve amounting to about 0.1 E.U./gram for a change in density (ρ_1) from 0.7 to 1.6 kg/L., the total entropy S_2 being ~1.5 to 2.0 E.U./gram. Since β 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 _{1.0}	$M\left(\frac{\mathrm{m/sec.}}{\mathrm{kg/1.0}}\right)$
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 α , v curve gives $(\partial \alpha / \partial v_2)_s$ with sufficient accuracy in the $\alpha(v)$ approximation.

Figure 1 presents the α , 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 α from either the dotted or solid curve are about the same order of magnitude (≤ 3 percent) as the experimental error involved in the measured detonation



¹⁸ R. L. Scorah, J. Chem. Phys. 3, 425 (1935).