

TABLE II. Equation of state relations from Fig. 1.

$\rho_2(\text{kg}/1.0)$	$v_2(1.0/\text{kg})$	$\alpha(1.0/\text{kg})$	$(d\alpha/dv_2)_S$
0.8	1.25	0.75	0.30
1.0	1.0	0.68	0.39
1.2	0.837	0.62	0.47
1.4	0.714	0.56	0.53
1.6	0.625	0.51	0.59
1.8	0.555	0.47	0.65
2.0	0.50	0.43	0.69
2.2	0.455	0.39	0.73

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.

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

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 α 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 α 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 α .

The equation of state employed by Kistiakowsky and Wilson⁸ based on Bridgman's equation of state is very convenient for studying the magnitude of $(\partial E/\partial v)_T$. In the equation

$$pv = nRT(1 + xe^x). \quad (20)$$

Kistiakowsky and Wilson took $x = K/T^2v$. For

the present purposes, however, the form

$$x = KT^c/v \quad (21)$$

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

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

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

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, $(\partial E/\partial v)_T \approx 2.1p_2c$. 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 β 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 β 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 Bullen¹⁹ 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

¹⁹ K. Bullen, Nature **157**, 405 (1946).

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

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 (ρ_2) up to 1.8 kg/L. Above 1.8 kg/L. it gives values of α 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,²¹ namely

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

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 α over the entire range shown. Even in the range of densities where Eq. (24) gives good agreement in α , it does not give good agreement in $(d\alpha/dv)$. Equation (26) on the other hand gives good agreement in both α 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

TABLE III. Detonation properties of various explosives.

*	ρ_1 kg/L.	D m/sec.	v_2 L./kg	α L./kg	β	n moles/kg	T_2 °K	W m/sec.	$p_2 \times 10^{-3}$ atmos.
PETN	1.0		0.725	0.546	0.65	35.2	5350	1540	85
PETN	BW	(5540)	(0.727)				(4130)	(1510)	(83)
PETN	1.2		0.615	0.488	0.58	35.0	5500	1660	125
PETN	BW	(6210)	(0.620)				(3960)	(1600)	(117)
PETN	R								(114)
PETN	1.2								
PETN	1.6		0.478	0.405	0.49	34.9	5700	1820	225
PETN	BW	(7650)	(0.477)				(3630)	(1800)	(218)
PETN	1.6		0.452	0.387	0.46	34.9	5800	1900	255
PETN	LS	(8400)	(0.439)					(2000)	(275)
RDX	1.0		0.723	0.545	0.64	40.5	5250	1660	95
RDX	BW	(5620)	(0.729)				(3980)	(1520)	(84)
	1.6		0.469	0.394	0.48	40.5	5750	2000	255
	BW	(7520)	(0.478)				(3570)	(1760)	(215)
TNT	1.0		0.740	0.570	0.65	33.1	3700	1250	60
TNT	BW	(4870)	(0.748)				(3170)	(1250)	(60)
TNT	1.6		0.505	0.447	0.48	24.5	4170	1340	150
TNT	LS	(7000)	(0.476)					(1680)	(190)
	BW	(7290)	(0.496)				3170	(1510)	(175)
Tetryl	1.0		0.752	0.573	0.71	37.0	4200	1340	75
	BW	(5440)	(0.740)				(3620)	(1420)	(75)
	1.6		0.485	0.415	0.50	35.5	4700	1670	200
	BW	(7720)	(0.486)				3380	1710	209
	1.63		0.473	0.407	0.49	35.5	4750	1720	210
	LS	(7600)	(0.465)					(1850)	(230)
Picric acid	1.0		0.746	0.572	0.68	36.2	3750	1290	65
	BW	(5190)	(0.745)				(3180)	(1340)	(69)
	1.6		0.489	0.422	0.49	35.0	4150	1550	180
	BW	(7680)	(0.492)				(3080)	(1640)	(199)
	1.63		0.478	0.412	0.48	35.0	(4200)	1610	190
	LS	(7100)	(0.465)					(1730)	(210)

* Data given in () are those computed by the investigators Brinkley and Wilson¹⁰—BW, Ratner⁷—R, and Landau and Stanyukovich⁸—LS.

²⁰ J. Hirschfelder, D. Stevenson, and H. Eyring, J. Chem. Phys. 5, 896 (1937).

²¹ H. Happel, Ann. d. Physik 4, 21, 242 (1905); R. Majumdar, Bull. Calcutta Math. Soc. 21, 107 (1929).