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Calculation of the Detonation Properties of Solid Explosives with the Kistiakowsky-Wilson Equation of State*

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The Kistiakowsky-Wilson equation of state, $pV_g=RT(1+xe^{\beta x})$, where $x=k/V_g(T+\theta)^{\alpha}$, for the gaseous detonation products of solid explosives has been re-examined in the light of new experimental data on detonation pressure and on the variation of detonation velocity D with loading density ρ_0 for several RDX/TNT mixtures. The value $\beta=0.30$ used in the past is too high to match the observed slopes of the $D-\rho_0$ curves. The old value $\alpha=0.25$ is too small to match the experimental Chapman-Jouguet pressure of most of these explosives, but too large to match the pressure of pure TNT. A suitable compromise for the explosives considered is $\alpha=0.5$, $\beta=0.09$, $\theta=400°$K.

1. INTRODUCTION

A NUMBER of attempts have been made in the past to calculate the detonation properties of solid explosives.[1-12] Since the gaseous detonation products develop pressures of the order of a quarter megabar ($1\text{ Mb}=10^{12}\text{ dynes/cm}^2=0.98692\times10^6$ atmos), directly applicable equation-of-state data are nonexistent and some form of theoretical or empirical equation of state for the detonation products must be assumed. When the investigations quoted in the aforementioned were made the only reliable experimental data available for comparison with the calculated results were detonation-velocity measurements; such data do not provide a very sensitive test of the correctness of the assumed equation of state. Recently, however, accurate measurements of the detonation pressures of several explosives have been made at this laboratory.[13,14] We have employed this data in a reinvestigation of an empirical equation of state which was first proposed by Kistiakowsky, Wilson, and Halford[8] and which has been utilized extensively for detonation calculations.[9-12]

The Kistiakowsky-Wilson equation of state as slightly modified by us has the form

$$pV_g/RT=F(x)=1+xe^{\beta x},$$

where

$$x=k/V_g(T+\theta)^{\alpha},\quad k=\kappa\textstyle\sum_i x_ik_i. \tag{1}$$

Here V_g is the molar gas volume, x_i is the mole fraction of component i, and the sum extends over all chemical components of the gaseous mixture. The quantities α, β, κ, θ, k_i are empirical constants, the k_i having the nature of covolumes (i.e., a sort of excluded volume) as is shown by the equilibrium equation (5). The values $\alpha=0.25$ and $\beta=0.30$, which were chosen originally[8] to give agreement with the experimental data then available, have been used in all of the succeeding work with this equation of state. However, several different sets of values of the k_i have been determined from experimental data (see references 9–11 and 12. We have treated all of the parameters (α, β, κ, k_i's) as adjustable in an effort to determine a set which would make it possible to match a set of experimental data which includes both the variation of detonation velocity with loading density ($D-\rho_0$), and the Chapman-Jouget pressure (p_{CJ}) at high loading density for a group of five related explosives.

With the value $\theta=0$ which has been used in the past, it may easily be seen that the equation of state has a minimum in p *vs* T (for constant V_g and composition). With $\alpha=0.25$ and with values of V_g appropriate to the detonation region this minimum occurs near 0°K, but with $\alpha=0.5$ it moves up to 2000 or 3000°K. We have used the arbitrary value $\theta=400°$K for all values of α; this has proved to be large enough to eliminate the minimum throughout the volume region characteristic of plane detonations, and yet is small compared with the values of T encountered.

The calculations are complicated by the possible presence of solid carbon. We have assumed this to be present as graphite and treated its equation of state as known, using a form employed extensively at this laboratory:

$$p=p_1(V_s)+a(V_s)T+b(V_s)T^2, \tag{2}$$

where, with p in megabars and T in volts (i.e., in units

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* This work was performed under the auspices of the U. S. Atomic Energy Commission, and has been reported in greater detail in Los Alamos Report LA-1865 (classified, not available for general circulation).

[1] P. Caldirola, J. Chem. Phys. 14, 738 (1946).

[2] M. A. Cook, J. Chem. Phys. 15, 518 (1947).

[3] H. Jones and A. R. Miller, Proc. Roy. Soc. (London) A194, 480 (1948).

[4] S. Paterson, Research 1, 221 (1948).

[5] T. L. Cottrell and S. Paterson, Proc. Roy. Soc. (London) A213, 214 (1952).

[6] T. Kihara and T. Hikita, *Fourth Symposium (International) on Combustion* (Williams and Wilkins, Baltimore, 1953), p. 458.

[7] Cook, Keyes, Horsley, and Filler, J. Phys. Chem. 58, 1114 (1954).

[8] G. B. Kistiakowsky and E. B. Wilson, Jr., OSRD-114 (1941).

[9] S. R. Brinkley and E. B. Wilson, Jr., OSRD-905 (1942).

[10] S. R. Brinkley and E. B. Wilson, Jr., OSRD-1707 (1943).

[11] Kirkwood, Brinkley, and Richardson, OSRD-2022 (1943), Appendix A.

[12] E. A. Christian and H. G. Snay, NAVORD-[illegible] ([illegible]), (classified, not available); H. G. Snay and I. Stegun, NAVORD-1732 (1951), (classified not available).

[13] W. E. Deal (LASL) (to be published).

[14] R. E. Duff and E. Houston, J. Chem. Phys. 23, 1268 (1955).

of 11 605.6°K),

$$p_1(V_s)=-2.467+6.769\eta-6.956\eta^2+3.040\eta^3-0.3869\eta^4,$$
$$a(V_s)=-0.2267+0.2712\eta,$$
$$b(V_s)=0.08316-0.07804\eta^{-1}+0.03068\eta^{-2},$$

with $\eta=V_s^0(T^0)/V_s=\rho/\rho_0$ being the compression of the material relative to its normal crystal density of 2.25 g/cc. The numerical coefficients were obtained by fitting expression (2) to points on the shock Hugoniot of graphite[15] and to the compressibility and thermal expansion coefficient at normal density. The range of applicability is $0.95<\eta<2.5$, $0<T<2$.

2. THEORY

If solid carbon is considered, expressions are needed for the thermodynamic functions of both gas and solid phases; these may be derived by standard thermodynamic methods, and are summarized here.

For the gaseous component with equation of state (1),

$$E=\sum x_i(E^0-H_0^0)_i+\sum x_i(H_0^0)_i +RT[\alpha T(F-1)/(T+\theta)], \quad (3a)$$

$$S=\sum x_i(S^0)_i-R[\sum x_i \ln x_i+\ln(p/p^0)] +R[\ln F-(e^{\beta x}-1)/\beta+\alpha T(F-1)/(T+\theta)], \quad (3b)$$

$$\mu_i=(F^0-H_0^0)_i+(H_0^0)_i+RT\ln(x_ip/p^0) -RT[\ln F-(e^{\beta x}-1)/\beta-\kappa k_i(F-1)/k], \quad (3c)$$

where the gas imperfection factor F is defined in Eq. (1) and should not be confused with the (Gibbs) free energies F^0 and F_s'.

For the solid with equation of state (2),

$$E=(H^0-H_0^0)+H_0^0-(pV_s)^0 +\int_{V_s^0}^{V_s}[b(V)T^2-p_1(V)]dV, \quad (4a)$$

$$S=S^0+\int_{V_s^0}^{V_s}[a(V)+2b(V)T]dV, \quad (4b)$$

$$\mu=(F^0-H_0^0)+H_0^0+F_s', \quad (4c)$$

where

$$F_s'=pV_s-(pV_s)^0-\int_{V_s^0}^{V_s}[p_1(V)+a(V)T+b(V)T^2]dV.$$

For chemical equilibrium,

$$\ln\Pi_g(n_i)^{\nu_i}=\ln K_p(T)-(\textstyle\sum_g\nu_i)\ln(p/n_gp^0) +(\textstyle\sum_g\nu_i)\left(\ln F-\dfrac{e^{\beta x}-1}{\beta}\right) -\dfrac{\sum_g\nu_ik_i}{k}(F-1)-\dfrac{\nu_sF_s'}{RT}, \quad (5)$$

where

$$RT\ln K_p(T)=-\sum\nu_i(F^0-H_0^0)_i-\sum\nu_i(H_0^0)_i$$

(one such equation for each independent chemical reaction).

In Eqs. (3) to (5) E, S, and μ are internal energy, entropy, and chemical potential, respectively. A superscript 0 refers to the reference state (ideal gas or real solid at pressure p^0 and temperature T),[16] with H_0^0 being the enthalpy of formation from the elements at absolute zero; x_i and n_i are the mole fraction and number of moles of component i; and $n_g=\sum_g n_i$. In Eq. (5) the ν_i's are the coefficients of the chemical reaction, positive for products and negative for reactants, and the subscript g for a sum indicates it is for gaseous components only.

The thermodynamic state of the detonation products is defined by the Hugoniot equation[17]

$$h\equiv E-E_0-\tfrac{1}{2}(p+p_0)(V_0-V)=0, \quad (6)$$

and the Chapman-Jouguet condition[18]

$$(\partial p/\partial V)_S=-(p-p_0)/(V_0-V). \quad (7)$$

In (6) the subscript 0 refers to the undetonated explosive, E_0 being given by the expression

$$E_0=(\Delta H_f)_e+\textstyle\sum_j N_j[H^0(T_0)-H_0^0]_j-p_0V_0, \quad (8)$$

where $(\Delta H_f)_e$ is the molar enthalpy of formation of the explosive at T_0, and N_j is the number of moles of element j in one mole of explosive.

3. CALCULATIONS

The detonation products were assumed to be made up of the following chemical components:

$$(1)\ H_2,\quad (2)\ CO_2,\quad (3)\ CO,\quad (4)\ H_2O,\quad (5)\ N_2,\quad (6)\ NO,\quad (7)\ C\ (\text{graphite}). \quad (9)$$

Oxygen was not included, since none of the explosives considered was more oxygen rich than RDX, which balances to N_2, H_2O, CO. In some preliminary calculations on IBM-CPC equipment some of the components considered by Brinkley, *et al.*,[10,11] *viz.*, NH_3, CH_4, and OH, were also included; these were found to be present in small though not negligible amounts. For

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[15] J. M. Walsh, private communication. The measurements were made by a dynamic method similar to that used for aluminum, copper, and zinc by J. M. Walsh and R. H. Christian [Phys. Rev. 97, 1544 (1955)].

[16] In evaluating the thermodynamic functions for the solid we neglected $(pV_s)^0$ and approximated $V_s^0(T)$ by $V_s^0(25°C)$. The resulting error was less than that of the analytic fits used for $(H^0-H_0^0)$ and S^0.

[17] See, for example, R. Courant and K. O. Friedrichs, *Supersonic Flow and Shock Waves* (Interscience Publishers, Inc., New York, 1948), p. 204.

[18] In the usual statement of the C−J condition, $(\partial p/\partial V)_S$ is to be evaluated for equilibrium composition. However, Kirkwood and Wood [J. Chem. Phys. 22, 1915 (1954)] have recently shown that this derivative should be evaluated with frozen composition. Our calculations have used the older statement of the C−J condition, but there is very little difference between the two, at least for our equation of state. Check calculations showed that the use of the correct C−J condition would decrease p_{CJ} by less than 1% at the lowest loading density of interest ($\rho_0=1.2$) and make almost no change at high loading density.

TABLE I. Heats of formation of the explosives.

Explosive	$(\Delta H_f)_e$ kcal/mole at 25°C
RDX (cyclotrimethylenetrinitramine)	+14.71[a]
TNT (trinitrotoluene)	−17.81[b]
$C_{3.3}H_{6.2}O_6N_{5.6}$[c]	+0.49[d]

[a] E. J. Prosen (NBS), (private communication).
[b] G. Stegeman, NDRC Division-8 Interim Report PT-7 (1943).
[c] Explosive presently classified.
[d] L. Sitney (LASL) (unpublished data).

the final calculations, however, the set (9) was used in order to simplify the solution of the equilibrium equations and thereby reduce the machine time required. Although this set is rather restricted, components of differing size (H_2, CO_2) and with positive heat of formation (NO) are included. It was found that with this set of components the determination of the equilibrium composition, given k, n_g, V_g, and T, could be reduced analytically to the solution of one equation in one unknown. (With solid carbon present this unknown was n_{CO}; with carbon absent, n_{H_2}.)

The required reference-state thermodynamic functions and enthalpies of formation were taken from the tables published by the National Bureau of Standards.[19] For calculational purposes, it was convenient to have the temperature-dependent data represented by analytic fits; the functions which we used have been given elsewhere.[20] The enthalpies of formation of the explosives are given in Table I.

The calculations were done on IBM 701 digital computers. It was found quite feasible to code a single problem to calculate adiabatic or Hugoniot curves, as well as detonation velocities. In order to produce points on these curves, Eqs. (1), (2), and (3b), (4b) (for an adiabat), or (6) (for a Hugoniot) were solved by iteration to obtain values of V and T for the desired S or $h(=0)$, with the composition given by Eqs. (5) and the mass balance relations. The detonation velocity was determined by finding the point on the Hugoniot where

$$D = V_0[(p-p_0)/(V_0-V)]^{\frac{1}{2}} \tag{10}$$

had its minimum value; this is equivalent to satisfying the C−J condition (7) with $(\partial p/\partial V)_S$ evaluated with equilibrium composition. The time required for the calculation of one adiabat or Hugoniot point was about 20 sec; for a detonation velocity, an average of about 140 sec.

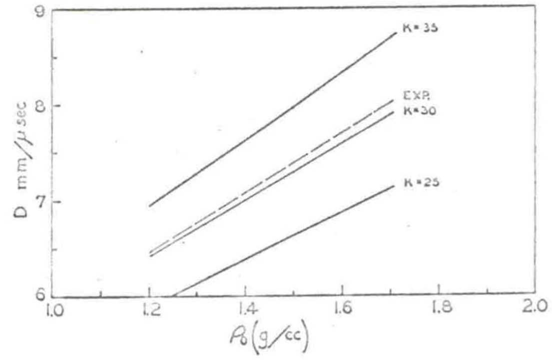

FIG. 1. The effect of κ on $D-\rho_0$; $\alpha=0.6$, $\beta=0.06$.

4. EFFECTS OF THE PARAMETERS

In order to determine the effects of the various equation-of-state parameters on the calculated $D-\rho_0$ curve and p_{CJ}, exploratory calculations were carried out for one explosive, 65/35 RDX/TNT. In order to save calculating time, these were carried out under the assumption of a fixed product composition resulting from the following decomposition equation:

$$C_qH_rO_sN_t = \frac{r}{2}H_2O + \left(s-\frac{r}{2}\right)CO + \left(q-s+\frac{r}{2}\right)C + \frac{t}{2}N_2. \tag{11}$$

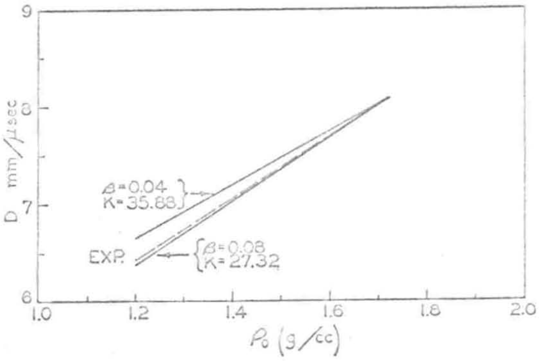

FIG. 2. The effect of β on $D-\rho_0$; κ chosen to match experimental D at one point; $\alpha=0.6$.

A set of geometrical covolume values was used, though with fixed composition the relative sizes of the individual k_i are unimportant. The other parameters were varied from the values

$$\alpha=0.6,\quad \beta=0.06,\quad \kappa=30, \tag{12}$$

which were found to give approximate agreement with the experimental $D-\rho_0$ and p_{CJ}. The results of the calculations are summarized in Figs. 1 through 5.[21]

Viewed from the standpoint of attempting to reproduce experimental data, the effects of the parameters

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[19] U. S. National Bureau of Standards, *Selected Values of Chemical Thermodynamic Properties, Series III* (loose leaf).

[20] W. Fickett and R. D. Cowan, J. Chem. Phys. 23, 1349 (1955).

[21] These parameter studies differ from the final calculations in that they used a more incompressible equation of state for carbon than that which was finally adopted and used in the main calculations. This "harder" equation of state was based on an interpolation between the static measurements of P. W. Bridgman [Proc. Am. Acad. Arts Sci. 76, 55–87 (1948)] and Thomas-Fermi-Dirac calculations made by R. D. Cowan at this laboratory (unpublished results).

may be pictured as follows: The value of κ may be changed to raise or lower the $D-\rho_0$ curve without greatly changing its shape (Fig. 1); β may then be used to change its shape and slope, while κ is varied so as to preserve a given value of D at one point (Fig. 2). Then the calculated C−J pressure may be changed by varying α, with β and κ always adjusted so as best to match $D-\rho_0$ (Figs. 3 and 4). Alpha also has a considerable effect on the C−J temperature (Fig. 3).[22] There exist no accurate experimental data on T_{CJ}, but it is noteworthy that the T *vs* ρ_0 curve for $\alpha=0.45$ is similar to that obtained at this laboratory from preliminary calculations with the Lennard-Jones-Devonshire free-volume equation of state.[23]

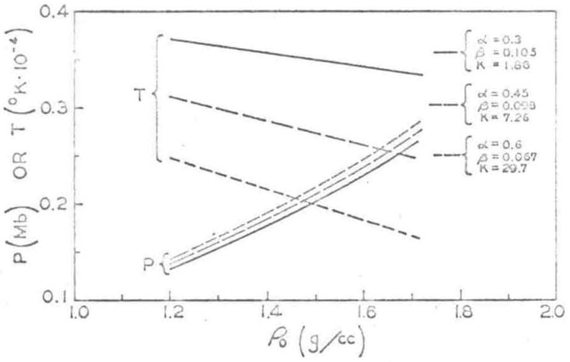

FIG. 3. The effect of α on p *vs* ρ_0 and T *vs* ρ_0; β and κ chosen to match experimental $D-\rho_0$.

In order to gain some idea of the effect of the carbon equation of state, calculations were made with the assumption that the carbon retained its normal volume, and also with the two equations of state for carbon mentioned earlier.[15,21] The results are shown in Fig. 5.

5. RESULTS

By assuming a fixed product composition and varying the parameters as described above, a set of values for α, β, and κ was found which gave results in good agreement with experiment for 65/35 RDX/TNT. It was found that with equilibrium composition (and the "geometrical" k_i discussed below) a not very different set also produced good agreement. The question of how well a single set of parameters could be made to serve for several explosives was then investigated.

The experimental data used were measurements of $D-\rho_0$ and of p_{CJ} at maximum loading density for a group of five related explosives. These data are given in Table II and were obtained as follows.

Measurements of the detonation velocity for infinite diameter, D_∞, were available [24–26] for each explosive at two densities, $\rho_0=1.2$ g/cc and the highest ρ_0 obtainable by pressing or casting. (Values of D_∞ were obtained by firing charges of different diameter d and extrapolating D *vs* $1/d$.) It was assumed on the basis of previous work, both at this laboratory and elsewhere, that over this range of loading density D *vs* ρ_0 could be represented by a straight line within experimental error.[27]

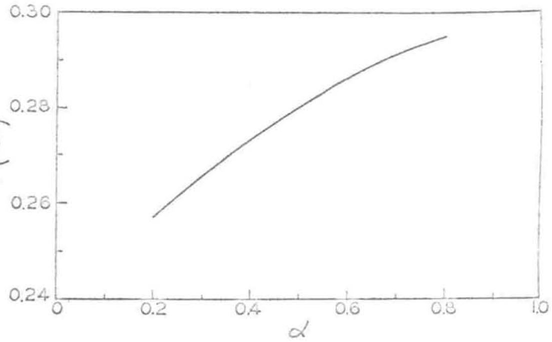

FIG. 4. The effect of α on p_{CJ} ($\rho_0=1.715$); β and κ chosen to match experimental $D-\rho_0$.

The Dural pressures in Table II were obtained from measurements of shock and free-surface velocities in Dural plates driven by the appropriate explosive.[13] The explosive C−J pressure p_i is given in terms of the metal pressure p_t by the matching conditions at the H.E.-metal interface:

$$\frac{p_i}{p_t}=\frac{1+R(\rho_{0i}D_i/\rho_{0t}D_t)}{1+R}, \tag{13}$$

where

$$R\equiv\rho_{0r}D_r/\rho_{0i}D_i$$

$$=\{(p_t-p_i)(v_0-v_i)/(v_i-v_t)(p_i-p_0)\}^{\frac{1}{2}}.$$

The subscripts i, r, and t refer to the incident, reflected,

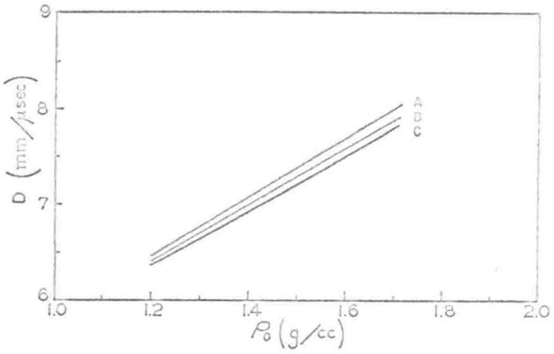

FIG. 5. Effect of the graphite equation of state on $D-\rho_0$: A—incompressible, B—graphite equation of state used in the parameter studies,[21] C—graphite equation of state used in the final calculations.[15] All curves are for $\alpha=0.6$, $\beta=0.06$, $\kappa=30$.

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[22] Such effects on the calculated pressure and temperature are also shown by a somewhat similar equation of state used by Cook *et al.*[7]

[23] W. W. Wood and W. Fickett (to be published).

[24] Campbell, Malin, James, Mautz, and Urizar (LASL), unpublished communications.

[25] Campbell, Malin, Boyd, and Hull (to be published).

[26] Campbell, Malin, and Holland (to be published).

[27] This assumption is being subjected to further investigation. While the experimental detonation velocities in Table II may be subject to slight revision, it is believed that they are accurate to within ±50 m/sec above $\rho_0=1.2$.

TABLE II. Experimental data for explosives.

Explosive and density for p_{CJ}	Detonation velocity[a] $D=A+B\rho_0$, (m/sec) A	B	Dural pressure[b] (Mb)	C−J pressure[c] (Mb)
RDX $\rho_0=1.800$	2515	3466	0.398	0.341
$C_{3.3}H_{6.2}O_6N_{5.6}$[d] $\rho_0=1.748$	2785	3233	0.378	0.316
78/22 RDX/TNT $\rho_0=1.755$	2702	3193	0.382	0.317
65/35 RDX/TNT $\rho_0=1.715$	2673	3127	0.358	(0.286)[e] 0.292
TNT[f] $\rho_0=1.640$	2360	2799	0.226	0.177

[a] Reference 24.
[b] Reference 13.
[c] See text.
[d] Explosive presently classified.
[e] Reference 14.
[f] More work on the TNT $D-\rho_0$ curve is in progress.

and transmitted shocks, respectively; the subscript 0 refers to material ahead of the shock. (All velocities are referred to the material ahead of the shock in question.) The value of R need not be known accurately, the so-called "acoustic approximation" $R=1$ giving results correct to within a percent or so. However, we have used values of R obtained by calculating shock curves for the detonation products.

The measurements of p_{CJ} and $D-\rho_0$ were taken on explosives of slightly differing composition and density, so all the data were corrected to the composition and density values in Table II by means of an error expression obtained by differential analysis of (13) with $R=1$, and by making use of the experimental dependence of D on composition and density:

$$\delta U_{fs}/U_{fs}=-0.86\delta\rho_0-0.0023\delta(\%\ \text{RDX}), \qquad (14)$$

in which U_{fs} is the experimentally measured free-surface velocity. All pressure values quoted in the table are believed to be accurate to 1 or 2%.

In attempting to determine a set of equation-of-state parameters from this experimental data, we started with a set of "geometrical" k_i (Table III) based on molecular sizes estimated from both virial-coefficient data and spherical volumes from bond lengths and van der Waals radii. Using these k_i in preliminary calculations it was found that $\alpha=0.5$, $\beta=0.09$, $\kappa=11.85$ would give $D-\rho_0$ and p_{CJ} close to the experimental values for 65/35 RDX/TNT. However, the agreement for other explosives was rather poor (Fig. 6). A least-squares process was therefore carried out (with this same α and β) to determine a set of k_i which would give the best agreement with all five explosives. Since the calculations indicated that the reaction $2CO \rightarrow CO_2 + C$ (graphite) shifts appreciably to the right as ρ_0 is increased, we allowed points of different ρ_0 for the same explosive to enter the least squaring on an equal weight with those from different explosives. Accordingly, the least squaring was carried out as follows:

TABLE III. Values of k_i.

Source	k_i H_2	CO_2	CO	H_2O	N_2	NO
Brinkley-Wilson[a]	153	687	386	108	353	233
"Geometrical"	180[b]	670	390	360	380	350
	2133[c]	7940	4622	4267	4505	4148
Least squares	2133	6407	3383	3636	6267	4148

[a] See references 9 to 11.
[b] Original set, chosen so that k_{CO} would be about the same as that used by Brinkley-Wilson.
[c] Scaled by the average κ (11.85) from the determination of all of the k_{obs} (see text).

Using a guessed set of k_i, a value of $k=\kappa\sum x_ik_i$ was determined at four loading densities (1.2, 1.4, 1.6, and maximum) for each of the five explosives by adjusting κ in each case until the calculated D was equal to the experimental value. If we designate these values of k as k_{obs} we then have a set of 20 linear equations for the set of k_i:

$$\textstyle\sum_i(x_i)_rk_i=(k_{obs})_r, \quad r=1,2,\cdots 20. \qquad (15)$$

These were solved by least squares for a new set of k_i.

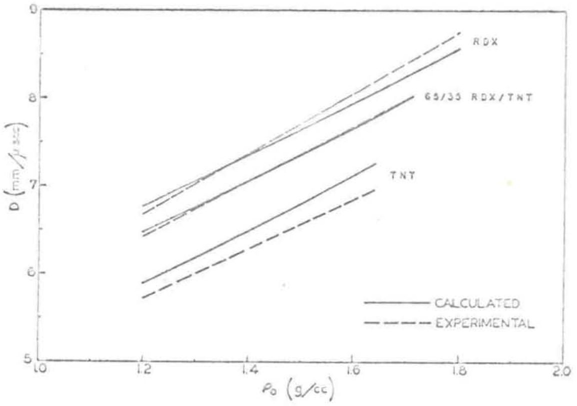

FIG. 6. Comparison of calculated and experimental $D-\rho_0$ curves for "geometrical" k_i; $\alpha=0.5$, $\beta=0.09$, $\kappa=11.8516$.

The first result of this process was large negative values for k_{H_2} and k_{NO}, probably because H_2 and NO were present in such small amounts. Therefore the equations were solved again with these two covolumes held constant at their original values (multiplied by the average κ from the determination of all of the k_{obs}). Table III contains the resulting k_i,[28] together with our "geometrical" set and the values obtained by Brinkley and Wilson.

In Figs. 6 and 7 the calculated results for $D-\rho_0$ are compared with experiment for both the geometrical and the least-square k_i. (To avoid confusion, results

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[28] In a preliminary trial of the least-squaring process on three explosives with $\alpha=0.6$ it was found that carrying out the entire least-squaring process a second time (starting with the k_i produced from the first least squaring) produced almost no change in the k_i. It was also found that the rather sizeable change in k_i from the initial geometrical set to the first least-square set produced composition changes of at most a few percent of the original mole fractions. Since the determination of so many k_{obs} is rather expensive in machine time, the final least squaring was started with the k_i from the above trial run and was done only once.

for only three explosives are shown; the others are qualitatively similar.) It can be seen that with the least-square k_i, fairly good agreement is obtained. The values of the parameters thus determined are

$$\begin{aligned} \alpha &= 0.5, \\ \beta &= 0.09, \\ \kappa &= 1.0, \\ k_i &= \text{least-square set, Table III.} \end{aligned} \tag{16}$$

The C−J pressures calculated with this set of parameters are compared with the experimental values in Table IV. The variation of C−J temperature and pressure with loading density for three explosives is shown in Fig. 8. The calculated variation in C−J composition with loading density for 65/35 RDX/TNT is shown in Fig. 9. (The compositions shown may not be physically meaningful, but the figure does serve to show the types of equilibrium shifts predicted by our calculations.)

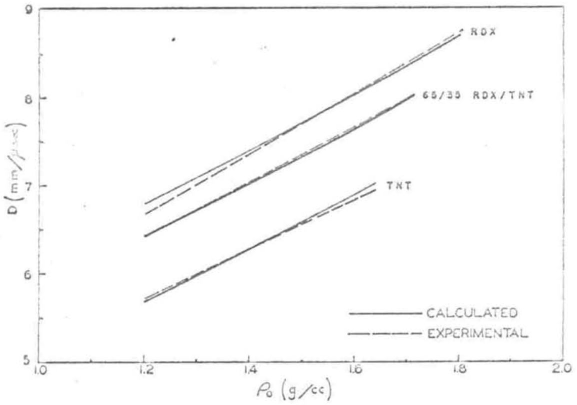

FIG. 7. Comparison of calculated and experimental $D-\rho_0$ curves for least-square k_i; $\alpha=0.5$, $\beta=0.09$, $\kappa=1$.

Table V gives (for 65/35 RDX/TNT) some points on the adiabat passing through the C−J point, and also points on the shock Hugoniot for the detonation products which originates at the C−J point. It can be seen that for all practical purposes the adiabat and shock curve are identical over the region which can be studied by the interaction of plane detonation waves with stationary metal plates.

6. DISCUSSION

As can be seen from Fig. 7 and Table IV the agreement with experiment is good in the case of D *vs* ρ_0, and, with the exception of TNT, fairly good in the case of p_{CJ}. The disagreement between calculated and experimental p_{CJ} for TNT is rather large. Perhaps a more enlightening comparison of theory and experiment[29] can be made

TABLE IV. Comparison of calculated and experimental results.

Explosive	C−J Pressure (Mb) Experimental	Calculated	Difference	γ^* Experimental	Calculated	V_g/V Calculated
RDX ($\rho_0=1.800$)	0.341	0.3488	+2.2%	3.05	2.908	0.0497
$C_{3.3}H_{6.2}O_6N_{5.6}$ ($\rho_0=1.748$)	0.316	0.3194	+1.1%	2.94	2.902	0.0633
78/22 RDX/TNT ($\rho_0=1.755$)	0.317	0.3106	−2.2%	2.82	2.899	0.0785
65/35 RDX/TNT ($\rho_0=1.715$)	0.292	0.2843	−2.8%	2.79	2.858	0.0945
TNT ($\rho_0=1.640$)	0.177	0.2066	+16.6%	3.48	2.913	0.1837

with a quantity related to the adiabatic compressibility:

$$\gamma_{CJ}^* \equiv -\frac{V}{p}\left(\frac{\partial p}{\partial V}\right)_S = \frac{\rho_0 D^2}{p_{CJ}} - 1. \tag{17}$$

[This expression can be obtained from Eqs. (7) and (10) by neglecting p_0.] The values of γ^* obtained from the experimental ρ_0, D, and p, together with the calculated values of γ^* and the calculated fraction of total volume occupied by graphite are shown in Table IV.

It can be seen that both calculated and experimental γ^*'s have a minimum as a function of the percentage of RDX. This is probably due to the large γ^* of carbon. As the percentage of RDX decreases, γ^* tends to be lowered by the decrease in pressure, but this tendency will be overcome by the increase in the amount of solid carbon present, if its γ^* is sufficiently high. Thus it might be expected that increasing the γ^* of the solid carbon would increase the calculated p_{CJ} for TNT more than for the other explosives. Accordingly, some calculations were made with the less compressible graphite equation of state,[21] whose γ^* at the TNT C−J point is 10.1 as compared with 5.65 for our graphite equation of state (2). However, this raised the γ^* of the product mixture by only 3% and hence lowered the calculated p_{CJ} for TNT by only 3%, while at the same time lowering the calculated p_{CJ} for 65/35 RDX/TNT by 1%.

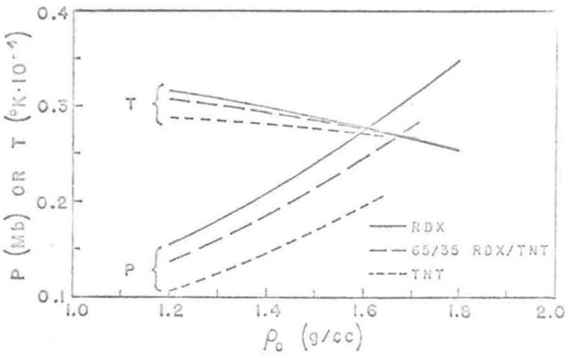

FIG. 8. Chapman-Jouguet pressure and temperature calculated with the final set of parameter values, (16).

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[29] A similar comparison can be made for a quantity

$$\alpha^* \equiv (\partial E/\partial pV)_p^{-1} = \{(\gamma^*+1)/(1+d\ln D/d\ln\rho_0)\}-2$$

discussed by H. Jones [*Third Symposium on Combustion and Flame and Explosion Phenomena* (Williams and Wilkins, Baltimore, 1949), p. 590]. The agreement is again singularly poor in the case of TNT.

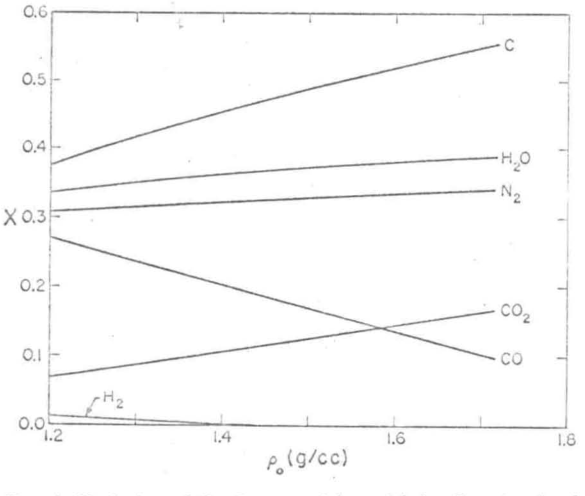

FIG. 9. Variation of C−J composition with loading density for 65/35 RDX/TNT. For the gaseous components the ordinate x is the mole fraction n_i/n_g; for carbon, x is n_s/N_C, the fraction of the total amount of carbon which is present as graphite.

Thus it appears to be unlikely that the large disagreement between the calculated and experimental p_{CJ} for TNT can be due to having the wrong γ^* for graphite. Although this disagreement remains unexplained, several calculations were done to see if a set of parameters could be found which would produce agreement with the experimental data for TNT only. It was found that with $\alpha=0$ (β and κ being adjusted to match experimental $D-\rho_0$), the calculated and experimental values of p_{CJ} for TNT agreed to within 2%. Agreement could also be obtained by taking $\alpha=0.25$ and assuming that the graphite was present in such a finely divided state that its heat of formation relative to that of the bulk material was +20 kcal/mole. However, both of these assumptions produced serious disagreement with experiment in the case of the other four explosives.

Table VI compares C−J quantities calculated with a number of different equations of state. With the exception of Paterson's, these equations of state all contain some adjustable parameters which have been evaluated with the aid of experimental $D-\rho_0$ data. The wide variation in the calculated $D-\rho_0$ relation is due in large part to differences in the experimental data obtained from various sources. Since the calculated pressure depends strongly on the detonation velocity [see Eq. (17)], comparisons are perhaps more appropriately based on the purely thermodynamic quantities γ^* and α^* than on the hydrodynamic pressure. Upon any basis the data in Table VI are notable mainly for variety rather than consistency. However, the most extreme values, namely, those due to Cook, Caldirola, and Paterson, are associated with equations of state such that $(\partial E/\partial v)_T = T(\partial p/\partial T)_v - p$ is zero. Thus these equations do not provide for any potential energy of molecular interaction; this can hardly be physically accurate since the densities concerned are greater than those of the undetonated solid explosive. The obvious result is excessively large thermal energies, hence the high C−J temperatures calculated by these authors.[30]

TABLE V. Adiabat and shock Hugoniot through the C−J point 65/35 RDX/TNT ($\rho_0=1.715$ g/cc).

	Adiabat		Shock Hugoniot	
V/V_0	p	γ^*	p	R(Eq. 13)
0.600	0.5316	2.98	0.5344	1.259
0.625	0.4710	2.96	0.4723	1.202
0.650	0.4195	2.94	0.4201	1.151
0.675	0.3755	2.93	0.3757	1.104
0.700	0.3377	2.91	0.3377	1.063
0.725	0.3050	2.90	0.3050	1.025
0.743 (CJ)	0.2843	2.89	0.2843	1.000
0.750	0.2765	2.89		
0.800	0.2297	2.85		
0.900	0.1646	2.81		
1.000	0.1227	2.76		
1.2	0.0746	2.69		
1.4	0.0495	2.62		
1.6	0.0350	2.55		
1.8	0.0260	2.50		
2.0	0.0201			

TABLE VI. Comparison of calculated[a] C−J quantities ($\rho_0=1.6$ g/cc).

Explosive	Source	D (m/sec)	$dD/d\rho_0$	T (°K)	p (Mb)	γ^*[Eq. (17)]	α^* (Fn. 29)
RDX	Experimental	8060	3470	...	0.265[b]	2.92[b]	0.32
	This paper	8037	3250	2788	0.273	2.79	0.30
	Brinkley-Wilson[e]	7520	3120	3570	0.218	3.15	0.49
	Cook[d]	8040	∼3570	5750	0.258	3.01	∼0.34
TNT	Experimental	6840	2800	...	0.168[b]	3.44[b]	0.68
	This paper	6894	3120	2715	0.196	2.88	0.25
	Brinkley-Wilson[e]	7290	4900	3170	0.178	3.78	0.30
	Cook[d]	7030	∼3660	4170	0.152	4.20	∼0.84
	Caldirola[c]	6900	2780	4030	0.212	2.59	0.18
	Jones-Miller[f]	7480	5260	3300	0.175	4.12	0.41
	Kihara-Hikita[g]	6950	3440	2270	0.195	2.96	0.21
	Paterson[h]	6790	3310	3900	0.127	4.81	1.26

[a] Some of the entries are approximate only, involving graphical interpolation or extrapolation from data for other loading densities.
[b] Estimated from the values in Table II with the aid of (17) and our calculated variation of γ^*+1 with ρ_0.
[c] See reference 10.
[d] See reference 2.
[e] See reference 1.
[f] See reference 3.
[g] See reference 6.
[h] See reference 4.

In summary it may be said that the Kistiakowsky-Wilson equation of state is perhaps as satisfactory as any which has yet been proposed, insofar as agreement between calculated results and experimental data is concerned. However, its calculated value for the C−J pressure of TNT leaves a good deal to be desired, and it has other unattractive features as well. The results obtained with the geometrical k_i (Fig. 6), and the rather different set of k_i (Table III) required to give agreement with experiment, indicate that *a priori* estimation of the covolumes is likely to be unsatisfactory and extensive least squaring together with additional experimental data would be required for the introduction of any new chemical components into the detona-

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[30] S. R. Brinkley, Jr., J. Chem. Phys. 15, 113 (1947).

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γ^*[Eq. (17)]	α^* (Fn.29)
2.92^b	0.32
2.79	0.30
3.15	0.49
3.01	~0.34
3.44^b	0.68
2.88	0.25
3.78	0.30
4.20	~0.84
2.59	0.18
4.12	0.41
2.96	0.21
4.81	1.26

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tion products considered. Also, analytical examination of Eq. (1) reveals that as V_g is decreased the minimum in p *vs* T at constant V_g will again occur. This unphysical behavior reduces confidence in the equation of state, particularly if it is to be extended to smaller volumes.

This equation of state is probably fairly reliable if its use is restricted to explosives which are similar to those included in a determination of its parameters, and to pressures and volumes not too different from those existing at the Chapman-Jouguet point. There would seem to be little justification for its use in an extended extrapolation of any sort.

An investigation similar to the one reported here using the Lennard-Jones-Devonshire free-volume equation of state is in progress at this laboratory.[23] Results will be published at a later date.

7. ACKNOWLEDGMENTS

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Rate of Recombination of Radicals.* I. A General Sector Theory; A Correction to the Methyl Radical Recombination Rate

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We have derived a rotating sector theory applicable to simple photochemical decompositions involving both first-order and second-order removal of radicals. This theory gives the behavior of radicals under intermittent illumination as a function of two parameters: α, the ratio of first- to second-order removal rates, and β, a function of flash time. We use this theory to recalculate the experimental data on the methyl radical recombination rate. We find the constant k_2 to be 2.2×10^{13} cc moles^{-1} sec^{-1} in the temperature range 125°C to 175°C.

1. INTRODUCTION

In this laboratory we have undertaken the further study of the recombination rates of radicals by the rotating sector technique, using ketones as the radical sources. To account properly for the steps involving first-order removal of radicals, we have reinvestigated the sector theory, deriving complete equations whose form is a simplification over previous work. These equations apply not only to ketones, but to a rather general gas phase photochemical mechanism. In this paper we present the theory and use it to correct the recent results obtained for the methyl radical recombination rate. The following paper presents results on the recombination of trifluoromethyl radicals. A future paper will present results on the recombination of ethyl radicals.

If, in a photochemical decomposition, the steady-state concentration of a certain radical is proportional to the square root of the absorbed light intensity, the recombination rate of these radicals may be studied by photolyzing under intermittent illumination (conveniently produced by a rotating sector whose dark to light ratio is p), for then the steady state concentration will vary from $(p+1)^{-1}$ to $(p+1)^{-\frac{1}{2}}$ times the unsectored value, as the sector speed varies from zero to infinity. Assuming simple square root dependence (removal of radicals only by recombination) Dickinson[1] and others[2,3] have developed a complete theory. Assuming one first-order (in radicals) removal step, O. K. Rice[4] and others[5,6] have developed theories. We present a new treatment applying to a general mechanism, and offering simplified final equations.

2. THEORY

Consider the following gas phase mechanism:

$$\begin{array}{rll} K\rightarrow m\mathrm{M}\cdot+\mathrm{CO} & \phi I_a & \\ 2\,\mathrm{M}\cdot\rightarrow P_{b1} & k_{b1}\text{ bimolecular} & \\ \cdots\cdots\cdots\cdots & & \\ 2\,\mathrm{M}\cdot\rightarrow P_{bi} & k_{bi} & \\ \mathrm{M}\cdot+A_1\rightarrow P_{f1} & k_{f1}\text{ first order} & (1)\\ \cdots\cdots\cdots\cdots & & \\ \mathrm{M}\cdot+A_i\rightarrow P_{fi} & k_{fi} & \\ \mathrm{M}\cdot+B_i\rightarrow P_{ci}+M\cdot & k_{ci}\text{ chain} & \end{array}$$

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