AN EQUATION OF STATE FOR THE DETONATION
OF CONDENSED EXPLOSIVES

INTRODUCTION

Hirschfelder and Roseveare proposed a state equation, for high temperature and pressure, in the virial form, with expansion in terms of $V$, in which the second virial coefficient is as usually determined, in the theory of slightly imperfect gases, and higher coefficients, third and fourth are retained in terms of the second, as found out by Boltzmann Happel, and others, for non-attracting rigid spheres. The fifth virial coefficient is assigned a value, chosen so that for small values of the volume, the equation may approximate the behaviour of closely packed spheres.

Paterson applied this equation of state to the detonation of condensed explosives. Recently there have been some attempts by De Boer and Michels, and Montroll and Mayer, to evaluate the cluster integral, relating to the third virial coefficient, directly in terms of the Lennard-Jones spherical potential.

Corner making use of these results, calculated the high temperature coefficients for various gases, and applied the state equation thus obtained, to the investigation of the properties of propellants. The present is an attempt to extend the validity of this state equation, to higher pressure regions, and to apply the results to the investigation of detonation parameters of condensed explosives. This necessitates the evaluation of another virial coefficient. Due to the inherent difficulty of calculating this in terms of the Lennard-Jones potential, it was chosen to find out its value, from the experimental data on explosives, by the application of the
hydrodynamic theory of detonation, by an inverse approach. The oxygen balanced explosive PETN, admits of such a possibility, for its products are mainly determined by the water gas equilibrium, and there is no change in the number of gm. moles of the products, with pressure or temperature.

**FUNDAMENTAL EQUATIONS**

Let the state equation for the mixture of the products of detonation, be expressed in the form

$$\frac{pV}{nRT} = (h_0 + \psi)$$

where $h_0$ is the factor known from Corner's results, and $\psi$ as a function of $V$ is to be determined.

$$h_0 = 1 + \frac{nb}{V} + \frac{n_c}{V^2}$$

$b$ and $c$ being the coefficient of the mixture.

$$nb = \Sigma n_i B_i \quad n_c = \Sigma n_i C_i$$

$B_i$ and $C_i$ being the coefficients for the individual gases. If $x$, $y$, $z$ and $w$ are the number of gm. atoms of carbon, hydrogen, oxygen and nitrogen in the original explosive, and the products are controlled by the water gas reaction, the number of gm. moles of carbon dioxide are given by the quadratic equation,

$$x^2(K-1) + x\left[K(x + y) - 3\right] + x(x-3) = 0$$

$K$ being the equilibrium constant. The amount of other gases becomes known from the equation, of conservation of atomic types. Proceeding along these lines, we have the composition for temperature $T = 4000^\circ K$ given by
\[ \text{CO}_2 = 3.226; \text{CO} = 1.775; \text{H}_2\text{O} = 3.775; \text{H}_2 = 0.226; \]
\[ N_2 = 2.00. \]

Making use of Corners' tables, we have
\[ \sum n_i B_i = 3.4603 \times 10^2 = nb \]
\[ \sum n_i C_i = 2.4533 \times 10^3 = nc \]

Therefore
\[ n = 11.0 \]
\[ n_c = 2.6986 \times 10^4 \]
\[ b = 31.46 \]
\[ c = 223.03 \]

From (42) we have
\[ \psi = \frac{PV}{nRT} - 1 - \frac{nb}{V} - \frac{n_c}{V^2} \]  
(50)

Differentiating wrt \( V \), we get
\[ \frac{d\psi}{dV} = \frac{1}{nRT} \left[ \psi \left( \frac{dP}{dV} \right)_H + P \right] - \frac{PV}{nRT^2} \left( \frac{dT}{dV} \right)_H \]
\[ + \frac{nb}{V^2} + \frac{2n_c}{V^3} \]  
(51)

the suffix \( H \) meaning that the differentiation is along the Hugoniot curve.

(E-H) of the RH equation for the oxygen balanced explosive, is expressible over a wide range of temperature as

\[ (E-H) = I_o T - H_o \]  
(52)

\( I_o \) and \( H_o \) being constants having dimensions of specific heat and energy, respectively given by
\[ I_o = 1151 \text{ Kcal. deg.}^{-1} \text{ (mole of PETN)}^{-1} \]
\[ H_o = 528.1 \text{ Kcal. (mole of PETN)}^{-1} \]

(These values are as given by Cottrell and Paterson)
The RH equation therefore becomes,
\[ I_o T - H_o = \frac{1}{2} p(V_o - V) \] (53)

Differentiating (53) we have,
\[ \left( \frac{dT}{dV} \right)_H = \frac{1}{2 I_o} (V_o - V) \left( \frac{dp}{dv} \right)_H - \frac{p}{2 I_o} \] (54)

Substituting (54) in (51) we get
\[ \left( \frac{dv}{dV} \right) = \frac{\left\{ \frac{V (dp)}{dv}_H + P \right\} 2 I_o}{\frac{RT}{N R}} \left[ \frac{V - V_o}{2 I_o} \left( \frac{dp}{dv} \right)_H - \frac{p}{2 I_o} \right] \]
\[ + \frac{\frac{n b}{v^3}}{v} + \frac{\frac{2 n c}{v^2}}{v} \] (55)

Eliminating \( \left( \frac{pV}{RT} \right) \) with the help of (48) we have
\[ \left( \frac{dv}{dV} \right) = \frac{2 I_o \left\{ V \left( \frac{dp}{dv} \right)_H + P \right\} - (2 \omega + V) \left( \frac{dp}{dv} \right)_H - P}{2 \frac{RT}{N R} \left[ V - V_o \right] + 2 H_o} \] + \frac{P}{V} \]
(56)
\[ q_o = \frac{\frac{n b}{v}}{v} + \frac{\frac{2 n c}{v^2}}{v} \]
The Chapman Jouguet condition is given by
\[ \left( \frac{dp}{dv} \right)_H = - \frac{p}{V_o - V} \] (57)

This enables \( \frac{dp}{dv} \) from (56) to be eliminated leading to the equation,
\[ \left( \frac{dv}{dV} \right) = \frac{2 I_o \left\{ \frac{pv}{V_o - V} + P \right\}}{2 \frac{RT}{N R} \left[ V - V_o \right] + 2 H_o} \]
(52)

The experimentally determined quantity is the detonation velocity. Therefore before the above equations can be usefully employed, the pressure \( p \) has to be eliminated. For that we make use of the relation,
\[ \rho^* = \frac{p}{(V_o - V)^m} \] (58a)
m being the molecular weight of the explosive. Putting the value of \( p \) from this relation in (58) we have
We define the following dimensionless variables

\[ \xi = \frac{v}{V_0}, \quad \eta = \frac{H_0}{m p^2}, \quad \phi = \frac{n R}{l_0} \]

With this (59) becomes

\[ V_0 \left( \frac{d\psi}{d\xi} \right) = \frac{2 (-2 \xi) + \eta}{\phi \left[ (-\xi)^2 + 2 \eta \right]} + \frac{2 (H_0 + \psi) (-\xi) + \xi^2 \eta}{\left[ (-\xi)^2 + 2 \eta \right]} + \frac{\eta}{\phi} \]

Now

\[ \frac{d\psi}{d\xi} = \frac{d\psi}{d\xi} \cdot \frac{d\xi}{d\xi} \]

Therefore

\[ \frac{d\psi}{d\xi} = \frac{d\psi}{d\xi} \left( V_0 + \xi \right) \cdot \frac{dV_0}{d\xi} \]

\[ = \theta + \frac{\theta}{V_0} \]

Elimination of \( T \) and \( p \) between (48), (52) and (58) provides another relation in terms of the dimensionless variables namely,

\[ \phi (H_0 + \psi) \left[ (-\xi)^2 + 2 \eta \right] + 2 \xi (\xi - 1) = 0 \]

(61) and (62) are the two equations giving two relation between \( \psi \) and \( \xi \) from which \( V_0 \) can be eliminated, and \( \psi \) found out. There is however no a priori information available on \( V_0 \) vs \( \xi \) relation, to enable (61) to be
integrated. In order to proceed towards solution we put,
\[ \psi = \frac{\eta d}{V^2} \tag{63} \]
as a first approximation. LHS of (59) is now given by
\[ \frac{d\psi}{dV} = -\frac{3\eta^2}{V^2} \]
\[ \therefore \frac{d\psi}{dV} = -\frac{3\eta^2}{V^3} = -\frac{3\psi}{\xi} \]
We have
\[ -\frac{3\psi}{\xi} = \frac{2(1-2\xi)}{\phi[(1-\xi)^2 + 2\eta]} + \frac{2(h_0 + \psi)(1-\xi)}{(1-\xi)^3 + 2\eta} + \frac{\eta}{\xi} \]
or
\[ 2\xi \phi(h_0 + \psi)(\xi - 1) - \phi(3\xi + 3\psi)\left[(1-\xi)^3 + 2\eta\right] \]
\[ + 2\xi(3\xi - 1) = 0 \tag{64} \]
This combined with (62) while giving \( \psi \) vs \( V \) solution, also
provides \( \eta \) vs \( \xi \) and \( V_0 \) vs \( \xi \) relations. The solution is obtained by
trying different values of \( V \) at a particular loading density, till the same
value of \( d \) is given by the two equations. For example at \( \xi_0 = 1.00 \text{ gms}, \)
per cc the following values were obtained,
\[
\begin{align*}
V_0 & = 316.2 \\
V & = 238.2 \\
\phi & = 0.1867 \\
\eta & = 0.2266 \\
\xi & = 0.7533 \\
(\xi - 1)^2 + 2\eta & = 0.5136 \\
2\xi(\xi - 1) & = -0.3706 \\
h_0 + \psi & = 2.9253 + 9.5113 \times 10^{-5}d \\
\phi(h_0 + \psi) & = 0.5462 + 1.8310 \times 10^{-5}d
\end{align*}
\]
Therefore equation (62) gives,
\[ d = 0.0957 \times 10^5 \]
\[(\% + 3\psi) = 2.3977 + 29.4339 \times 10^{-5} d\]
\[\phi (\% + 3\psi) = .4480 + 5.4953 \times 10^{-5} d\]
\[2\xi(2\xi-1) = .7674\]

With this the equation (64) leads to,
\[d = .0957 \times 10^{-5}\]

The complete solution is tabulated below.

<table>
<thead>
<tr>
<th>Loading density (\rho) gms./cc.</th>
<th>Volume (V_0)</th>
<th>Volume (V)</th>
<th>(\xi)</th>
<th>(\eta)</th>
<th>(d \times 10^{-5})</th>
</tr>
</thead>
<tbody>
<tr>
<td>.25</td>
<td>1264.8</td>
<td>840.1</td>
<td>.6642</td>
<td>.6649</td>
<td>.968</td>
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<tr>
<td>.50</td>
<td>632.4</td>
<td>441.6</td>
<td>.6983</td>
<td>.4589</td>
<td>.204</td>
</tr>
<tr>
<td>.75</td>
<td>421.6</td>
<td>308.3</td>
<td>.7313</td>
<td>.3133</td>
<td>.134</td>
</tr>
<tr>
<td>1.00</td>
<td>316.2</td>
<td>238.5</td>
<td>.7543</td>
<td>.2266</td>
<td>.096</td>
</tr>
<tr>
<td>1.50</td>
<td>210.8</td>
<td>167.2</td>
<td>.7932</td>
<td>.1209</td>
<td>.075</td>
</tr>
<tr>
<td>1.72</td>
<td>183.8</td>
<td>147.3</td>
<td>.8014</td>
<td>.1013</td>
<td>.059</td>
</tr>
</tbody>
</table>

The difference between the experimental value of the detonation velocity and that calculated for a constant value of the fourth virial coefficient is reflected in the variation of the value of \(d\) thus obtained.

**Comparison of \(d\) with the value of the fourth virial coefficient calculated for non-attracting rigid spheres**

The value of the fourth coefficient \(0.287 \left( \sum n_i B_i \right)^3\), in Boltzmann's equation corresponds to \(n^3 \sum n_i D_i\), in the present case.

We have
\[\sum n_i D_i = nd\]
\[ n^3 d = n^3 \sum \gamma_i \delta_i. \]
\[ \frac{\Sigma \gamma_i \delta_i}{n} = b \quad \text{for the mixture} \]
\[ 0.287 \left[ \frac{\Sigma \gamma_i \delta_i}{n} \right]^3 = 0.287 n^3 b^3 \]
\[ d = 0.287 b^3 \]

From the composition already found out by water gas equilibrium at 4000\(^\circ\)K, we have from tables.

\[ b = 31.457 \]
\[ d = 0.093 \times 10^5 \]

This corresponds to about the middle of the above table.

Logarithmic plot of \( V_o \) and \( \xi \) values given below, gives a straight line, shown in Figure 4, giving the following relation between \( V_o \) and \( \xi \),

\[ V_o = 16.92 \xi - 10.417 \]

**Table 2**

<table>
<thead>
<tr>
<th>( \xi )</th>
<th>0.6642</th>
<th>0.6983</th>
<th>0.7313</th>
<th>0.7543</th>
<th>0.7932</th>
<th>0.3044</th>
</tr>
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<tbody>
<tr>
<td>( \log \xi )</td>
<td>1.8223</td>
<td>1.8441</td>
<td>1.8641</td>
<td>1.8776</td>
<td>1.8994</td>
<td>1.9038</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( V_o )</th>
<th>1264.8</th>
<th>632.4</th>
<th>421.6</th>
<th>316.2</th>
<th>210.2</th>
<th>183.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log V_o )</td>
<td>3.1030</td>
<td>2.3010</td>
<td>2.6249</td>
<td>2.5000</td>
<td>2.3238</td>
<td>2.2645</td>
</tr>
</tbody>
</table>

Making use of this approximation, we have

\[ \frac{\Delta V}{\Delta \xi} = -16.92 \times 10^{-4} \xi - 11.417 \]
\[ \frac{\Delta V}{\Delta \xi} = \theta + \frac{\xi - 16.92 \times 10^{-4} \xi - 11.417}{16.92 \xi - 10^{-4} \xi} \]
\[ = -9.417 \theta \]
\[ = -9.417 \left[ \frac{2(1-\xi)}{\Phi(1-\xi)^2 + 2\gamma} + \frac{2(h+\psi)(1-\xi)}{(1-\xi)^2 + 2\gamma} + \frac{\gamma}{\xi} \right] \]

(65)
PLOT OF $\log \gamma$ AGAINST $\log \xi$.

For $\gamma = \frac{\tilde{\eta} d}{\tilde{\nu}^2}$.
This has been solved numerically as explained in the next section.

**SOLUTION OF THE EQUATION**

The equation has been integrated numerically at intervals of $\xi = 0.005$. To start the solution five values of the derivative $\psi'$, at equal intervals are needed. They have been found out by Milnes formulae. If $\psi'$ and $\psi''$ are the first and the second derivative of $\psi$ at the initial point, the values of the first derivatives $\psi'$, $\psi''$ at both sides of the origin at equal intervals, is as a first approximation given by,

$$
\psi_i' = \psi_o' + h \psi_o'' \\
\psi_i'' = \psi_o' - h \psi_o''
$$

We need $\psi'$ and $\psi''$ in order to calculate this, for which the initial conditions have to be known. These are given below:

**INITIAL CONDITIONS**

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>0.1 gms/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0$</td>
<td>3162 cc</td>
</tr>
<tr>
<td>$\psi$</td>
<td>0</td>
</tr>
<tr>
<td>$V_o$</td>
<td>16.98 $\xi$</td>
</tr>
<tr>
<td>$\xi$</td>
<td>6054 $\xi_0$</td>
</tr>
<tr>
<td>$V$</td>
<td>1914.3</td>
</tr>
<tr>
<td>$h$</td>
<td>1.1082</td>
</tr>
<tr>
<td>$q$</td>
<td>1.1956</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.0334</td>
</tr>
</tbody>
</table>
| $\frac{d\eta}{d\xi}$ | -6.1111 | From the graph of $\eta=\xi$ extrapolated to lower densities as shown in Figure 5.

With this

$$
\psi_o' = 2.55219
$$
\[ \eta \quad \text{Vs} \quad \xi, \quad \text{FOR} \quad \psi = \frac{n_d}{V^3} \]
Calculation of $\psi^* _1$:

$$
\psi^* _1 = -9.47 \frac{d}{d\xi} \left[ \frac{2(1-\xi^2)}{\phi[(1-\xi)^2+2\eta]} + \frac{2(h^0+\psi)(1-\xi)}{(1-\xi)^2+2\eta} + \frac{\tau}{\xi} \right]
$$

$$
\frac{d}{d\xi} \frac{2(1-\xi^2)}{\phi[(1-\xi)^2+2\eta]} = -4 \left[ \frac{(1-\xi)^2+2\eta}{\phi[(1-\xi)^2+2\eta]} \right] \frac{d(1-\xi)}{d\xi} + \frac{2(h^0+\psi)}{(1-\xi)^{3/2}+2\eta} \frac{d(1-\xi)}{d\xi}
$$

$$
\frac{d}{d\xi} \frac{2(h^0+\psi)(1-\xi)}{(1-\xi)^{3/2}+2\eta} = \left[ \frac{(1-\xi)^2+2\eta}{(1-\xi)^{3/2}+2\eta} \right] \frac{d(h^0+\psi)}{d\xi} - \frac{2(h^0+\psi)}{(1-\xi)^{3/2}+2\eta} \frac{d(1-\xi)}{d\xi}
$$

We have

$$
\frac{d\rho}{d\xi} = \frac{d\rho}{dV} \frac{dV}{d\xi} = V_0 + \frac{\tau}{\xi}, \quad \frac{dV}{d\xi} = -15.990 \times 10^{-4}
$$

$$
\frac{d\rho}{d\xi} = -2.9770 \times 10^4, \quad \frac{dV}{d\xi} = -1.0318 \times 10^4
$$

$$
\frac{d\rho}{d\xi} = 3.0419 \times 10^4, \quad \frac{dV}{d\xi} = 1.09911 \times 10^4
$$

$$
\frac{d\rho}{d\xi} = 3.2705
$$

With these values we have

$$
\psi^* _1 = 67.93254
$$

$\psi^* _1 = 2.55229 + 0.005 \times 67.93254$

$\psi^* _1 = 2.29195$

$\psi^* _1 = 2.21263$

We have $\psi$ and $\psi_1$ given by

$$
\psi^* _1 = \psi_0 + \frac{1}{24} \left( \psi_1 + \psi_1^* + 7\psi^*_1 \right) + \psi^*_0 \frac{\tau}{\xi} \quad \text{(A)}
$$

$$
\psi^* _1 = \psi_0 - \frac{1}{24} \left( 7\psi^*_1 + \psi_1^* + \psi^*_1 \right) + \psi^*_0 \frac{\tau}{\xi} \quad \text{(B)}
$$
Putting these values we have
\[ \Psi_1 = 0.013226 \]
\[ \Psi_{11} = -0.011915 \]

Putting these values of \( \Psi \) in the original differential equation, reading \( \eta \) from the graph improved values of \( \Psi' \) and \( \Psi_{11} \) or obtained. We get
\[ \Psi'_{1} = 2.88989 \]
\[ \Psi'_{11} = 2.21309 \]

These in turn are again put in the formulas (A) and (B) mentioned above, to get improved values \( \Psi \) and \( \Psi' \). These are again put in the differential equation to get better values of \( \Psi' \). This process is repeated till successive values of \( \Psi' \) agree. This gives there values of \( \Psi' \) to be used for starting the solution. Values of \( \Psi' \) at two more points are needed. For that we determine, the value of \( \Psi \) given by,
\[ \Psi_2 = \Psi_0 + \frac{h}{3} (5 \Psi' - \Psi'_{11} - \Psi'_{1}) - 2 \Psi_{11} h^2 \]
\[ \Psi_{21} = \Psi_0 - \frac{h}{3} (5 \Psi'_{11} - \Psi'_{1} - \Psi_{11}) - 2 \Psi'_{11} h^2 \]

So \( \Psi_2 \) and \( \Psi_{21} \) can be found out, for \( \Psi'_{1}, \Psi' \) and \( \Psi_{11} \) are now very accurately known.
\[ \Psi_2 = 0.028880 \]
\[ \Psi_{21} = -0.022139 \]

Putting these values again the differential equation we obtain.
\[ \Psi'_{2} = 3.28437 \]
\[ \Psi'_{21} = 1.88340 \]

To check the values of \( \Psi' \) and \( \Psi_{11} \) we have
\[ \Psi'_{2} = \Psi_0 + \frac{h}{3} (\Psi' + 4 \Psi_{11} + \Psi'_{1}) \]
\[ = 0.028994 \]
\[ \Psi'_{21} = \Psi_0 - \frac{h}{3} (\Psi'_{11} + 4 \Psi_{11} + \Psi'_{1}) \]
\[ = -0.022147 \]

Putting these values in the above differential equation, we get improved values of \( \Psi_{2} \) and \( \Psi_{21} \). These in turn can be put in the above, till successive values of \( \Psi' \) and \( \Psi_{11} \) agree. Proceeding like this we have
\[ \Psi'_{2} = 3.28399 \]
\[ \Psi_{21} = 1.88340 \]
Having thus got the value of $\psi$ at five points, the value at the next interval can be obtained by the formula

$$I_{n+1}^n = h \left[ \psi_n + \frac{1}{2} \Delta \psi_n + \frac{1}{2} \Delta_2 \psi_n + \frac{1}{3} \Delta_3 \psi_n + \frac{1}{4} \Delta_4 \psi_n \right]$$

Where $I_{n+1}^n$ denotes the increment in the function $\psi$ from the interval $n$ to $(n+1)$ and $\Delta \psi_n$ etc., are the successive differences of the function $\psi'$. Having got this new value of $\psi$, $\psi'$ at that point can be found out, and the use of the above formula repeated. Proceeding along these lines the values of $\psi$, for $\xi = .6054$ to .8054 obtained are given in Table 3. As the values of $\eta$ are read from the graph, the values of higher differences $\Delta \psi_n'$ become irregular. For that reason the number of figures given in the table are not a measure of the accuracy.

From (42) we have

$$\psi = \frac{2\xi (1-\xi) - \phi \eta \left[(1-\xi)^3 + 2\eta\right]}{\phi \left[(1-\xi)^3 + 2\eta\right]}$$

At a particular value of the specific volume, $\eta$ and $\phi$ get fixed, and a value of $\xi$, has to be found out, for which the above equation, and the $\psi(\eta)$ given in the table are simultaneously satisfied. This was determined by a graphical solution, for various values of $\xi$. A typical graph is shown in Figure 6.

The final $\psi$ vs $V$ relation is mapped out in Figure 7.

As would appear, this value of $V$ corresponds to the volume in the detonation front at the Chapman Jouguet point. By virtue of the relation (48) and (58a) the pressure and temperature at the CJ point can now be calculated. The results are given in the Table 4.

The relation between $\log \xi$ and $\log V$ is given in Table 5.

As shown in Figure (6), leaving aside the value of $V$ for may be represented by

$$\psi = \frac{5.74 \times 10^4}{V^2}$$
FIG. 6

$\psi \text{ Vs } \xi$

$\rho = 0.75$

$\xi = 0.7007$

$V = 295.42$

$\psi = 0.6564$
### Table 3

<table>
<thead>
<tr>
<th>$\xi$</th>
<th>$\psi$</th>
<th>$\xi$</th>
<th>$\psi$</th>
<th>$\xi$</th>
<th>$\psi$</th>
</tr>
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<td>0.6054</td>
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<td>0.6754</td>
<td>0.3807</td>
<td>0.7454</td>
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</tr>
<tr>
<td>0.6104</td>
<td>0.0132</td>
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<td>0.4281</td>
<td>0.7504</td>
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</tr>
<tr>
<td>0.6154</td>
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<td>1.762</td>
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<td>1.920</td>
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<td>0.0636</td>
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<tr>
<td>0.6454</td>
<td>0.1640</td>
<td>0.7154</td>
<td>0.8704</td>
<td>0.7854</td>
<td>2.904</td>
</tr>
<tr>
<td>0.6504</td>
<td>0.1917</td>
<td>0.7204</td>
<td>0.9579</td>
<td>0.7904</td>
<td>3.144</td>
</tr>
<tr>
<td>0.6554</td>
<td>0.2245</td>
<td>0.7254</td>
<td>1.0423</td>
<td>0.7954</td>
<td>3.390</td>
</tr>
<tr>
<td>0.6604</td>
<td>0.2604</td>
<td>0.7304</td>
<td>1.1400</td>
<td>0.8004</td>
<td>3.664</td>
</tr>
<tr>
<td>0.6654</td>
<td>0.2969</td>
<td>0.7354</td>
<td>1.2524</td>
<td>0.8054</td>
<td>3.943</td>
</tr>
<tr>
<td>0.6704</td>
<td>0.3370</td>
<td>0.7404</td>
<td>1.3660</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Loading density $\xi$ gm./cc.</th>
<th>Volume $V$ cc/gm.</th>
<th>$\psi$</th>
<th>Pressure $p \times 10^{10}$ dynes/cm$^2$</th>
<th>Temperature $T^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.25</td>
<td>2.616</td>
<td>.2144</td>
<td>.908</td>
<td>4917</td>
</tr>
<tr>
<td>.50</td>
<td>1.341</td>
<td>.3388</td>
<td>2.506</td>
<td>5045</td>
</tr>
<tr>
<td>.75</td>
<td>0.934</td>
<td>.6564</td>
<td>5.001</td>
<td>5155</td>
</tr>
<tr>
<td>1.00</td>
<td>0.724</td>
<td>1.042</td>
<td>8.544</td>
<td>5277</td>
</tr>
<tr>
<td>1.50</td>
<td>0.514</td>
<td>2.278</td>
<td>19.55</td>
<td>5491</td>
</tr>
<tr>
<td>1.72</td>
<td>0.453</td>
<td>2.603</td>
<td>26.22</td>
<td>5599</td>
</tr>
</tbody>
</table>
$\psi$ Vs $V$

FIG. 7
Before this result can be applied to other explosives, \( n \) - the number of gm. moles of the gaseous products has to be separated out. The volume per gm. mole is a property, through which the value of \( \psi \) thus found can be switched over to other explosives. This will entail the assumption that \( \psi \) remains the same function of \( \frac{V}{n} \), from one explosive to another. So we have

\[
\psi = 475.5 \left( \frac{n}{V} \right)^2
\]  

(66)

Thus the correction so found can be absorbed in the coefficient of \( V^{-2} \), thus leading to the following state equation, suitable for the investigation of other explosives,

\[
\frac{pV}{nRT} = 1 + 31.46 \left( \frac{n}{V} \right) + 698.5 \left( \frac{n}{V} \right)^2
\]  

(67)

It is interesting to note that \( \psi \) can be thus absorbed, in spite of the fact, that as a first approximation, it was put as a function of \( V^{-3} \). An examination of the Table I would reveal, that the variation in \( d \) is about the same, as the variation in \( V \) (except for the value of \( \xi = 0.25 \text{ gm./cc} \)), so that, even at that stage, it could have been put as a function of \( V^{-2} \), in which case \( d \) would be sensibly constant, in the specified volume range.

APPLICATION TO OTHER EXPLOSIVES

Having constructed the state equation thus, it can be applied to the investigation of other explosive.
Oxygen Positive Explosives

In this case the composition can be put straight from the constitution of the explosive. For nitroglycerine for example we have,

$$C_3H_5O_9N_3 \rightarrow 3CO_2 + 2.5 H_2O + .25 O_2 + 1.5 N_2 \quad (60)$$

From the heats of formation of nitroglycerine and that of the products we have,

$$H = 341.40 \text{ Kcal/gm. mole}$$

$$n = 7.25$$

At various temperatures $E$ can be found out from Pikes tables and thus $(E-H)$ determined. At a particular value of the temperature $T$ the volume has to be found out, that gives a correct value of $V_c$, as found out from RH equation. Finding a few values of the volume the curve of equation can be constructed. The curve was drawn with the following set of $pV$ values given in Table 6. The value of pressure $p$ and volume $V$ at the point of contact of the tangent, from the initial point, enable the detonation velocity $D$ to be determined by the relation,

$$D^2 = \frac{P}{(V_0 - V)w} V^2$$

$$= \frac{4.57 \times 10^{10} \times 10^{10}}{31.44 \times 227.1} \times 2.04 \times 10^5 = 53.90 \times 10^{13}$$

or

$$D = 7360 \text{ m/sec}.$$  

The best experimentally measured value is $7500 \pm 500 \text{ m/sec.}$


<table>
<thead>
<tr>
<th>$p$ Kcal./cc</th>
<th>2.42</th>
<th>2.98</th>
<th>3.52</th>
<th>4.03</th>
<th>4.57</th>
<th>5.24</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$ cc</td>
<td>137</td>
<td>127</td>
<td>120</td>
<td>115</td>
<td>110</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 6
Oxygen Negative Explosives:

For oxygen balanced explosives the composition is mainly determined by the water gas equilibrium, while for oxygen negative ones, some equilibria in addition to the water gas have to be considered. The presence of the solid phase, among the products of the later, introduces another unknown parameter. Before describing the detailed procedure for calculation relating to other explosives, it is worth while digressing a little, to consider the theory of chemical equilibrium.

Theory of Chemical Equilibrium:

A chemical reaction can be represented in a most general way by

\[ \Sigma n_i A_i = \Sigma n_j A_j \]  \hspace{1cm} (70)

meaning \( n_i \) moles of the species \( i \) and the like give rise to \( n_j \) moles of species \( j \) and the like. The condition of equilibrium for such a reaction is given by

\[ \Sigma n_i \mu_i = \Sigma n_j \mu_j \]  \hspace{1cm} (71)

\( \mu_i \) etc., being the chemical potential of the reactant \( i \) in the mixture defined by

\[ \frac{\delta G}{\delta n_i/\tau n_j} = \frac{\delta A}{\delta n_i/\tau n_j} ... \]  \hspace{1cm} (72)

\( G \) and \( A \) being the Gibbs and the Helmholtz free energy respectively. A quantity more fundamental than \( \mu_i \) is the absolute activity \( \lambda_i \) of the component \( i \) related to \( \mu_i \) by the relation \( \mu_i = RT \ln \lambda_i \). With this the condition of equilibrium can be represented by

\[ \pi(\lambda_i)n_i = \pi(\lambda_j)n_j \]  \hspace{1cm} or

\[ \frac{\pi(\lambda_i)n_i}{\pi(\lambda_j)n_j} = 1 \]  \hspace{1cm} (73)
denominator being the product of the absolute activities of all the reactants in the process, and numerator that of the products.

We have $\mu_i$, in the perfect gas condition given by

$$\mu_i = \mu_i^* + RT \ln \frac{p_i}{p_f}$$

(74)

$p_i$ being the partial pressure of the component $i$. The corresponding relation between the absolute activity $\lambda_i$ and the partial pressure $p_i$, therefore is

$$\lambda_i = \lambda_i^* \frac{p_i}{p_f}$$

(75)

$\lambda_i^*$ being the absolute activity for $i$ at some standard pressure $p_f$.

As we pass from considerations of perfect gases to imperfect ones, we define a quantity called the fugacity $p_i^*$ of the component $i$ in the mixture, defined by

$$\frac{p_i^*}{\lambda_i} = \text{Const.} \ (T \ \text{constant})$$

(76)

$$\frac{p_i^*}{p_c} \rightarrow 1 \ \text{as} \ p \rightarrow 0 \ (\text{all } T)$$

Thus for a real gas the relation corresponding to (74) for a perfect gas, mentioned above, is

$$\lambda_i = \lambda_i^* \frac{p_i^*}{p_f}$$

(77)

Putting down the relation (75) in (73) we have

$$\frac{\pi \left( \frac{p_i}{p_f} \right)}{\pi \left( \frac{p_i^*}{p_f} \right)} = K(T)$$

(78)

$$K^{-1}(T) = \pi(\lambda_i^*)$$

By virtue of the relation (77) we have for an imperfect gas instead
In order to determine the fugacity from the equation of state, we have

$$\pi \left( \frac{p^*}{p^*} \right) = K(T)$$  \hspace{1cm} (79)$$

$$\pi \left( \frac{p^*}{p^*} \right) = \int \left[ \left( \frac{\partial p}{\partial \mu} \right)_T - \frac{RT}{V} \right] dV - R \ln \frac{V}{V_0}$$  \hspace{1cm} (80)$$

We have from the equation (67),

$$\left( \frac{\partial p}{\partial \mu} \right)_T = \frac{\pi}{\mu} \left( 1 + \frac{n b}{V} + \frac{n c}{V^2} \right) = \frac{RT}{V} \left( 1 + \frac{n b}{V} + \frac{n c}{V^2} \right) + \frac{nRT}{V} \left( \frac{b}{V} + \frac{2n c}{V^2} \right)$$  \hspace{1cm} (81)$$

$$\frac{\partial p}{\partial \mu} \left|_{T,p,n} \right. = \frac{RT}{V} \int \left( \frac{\alpha n b}{V^2} + \frac{3\beta n c}{V^3} \right) dV - R \ln \frac{V}{V_0}$$  \hspace{1cm} (82)$$

We have

$$\Pi \left( \frac{p^*}{p^*} \right) = \Pi \left( \frac{p^*}{p^*} \right)$$  \hspace{1cm} (83)$$

$$\frac{\pi(n_i)}{\pi(n_j)} = \frac{V}{RT} \exp \left( -\frac{2nb}{V} + 1.5 \frac{n c}{V^2} \right) \times K(T)$$  \hspace{1cm} (84)$$

At a certain temperature T, and volume of the gaseous products having the total number of moles equal to n the composition is worked out from the equations of equilibrium assumed. At this temperature and volume, calculations are repeated, till the value of n, obtained, agrees with
that assumed for it. The final composition so determined, gives the amount and hence volume of carbon $V_c$ and therefore the total volume $V$. This final volume should lead to the right value of $V$, as found out from RH equation. Calculations are repeated at different temperatures, and the right value of $V$ and $p$ satisfying Hugoniot equation found out, and the curve drawn. The value of $p$ and $V$ at the tangent point, to this curve, enables to be determined by the relation (68).

Calculations for TNT

In order to determine the composition of the products the following equilibria, may be considered.

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} & = \text{CO}_2 + \text{H}_2 \quad \text{(54a)} \\
\text{C} + 2\text{H}_2 & = \text{CH}_4 \quad \text{(54b)} \\
2\text{CO} & = \text{CO}_2 + \text{C} \quad \text{(54c)}
\end{align*}
\]

If $K_1$, $K_2$, and $K_3$ are the equilibrium constants for these reactions, in case the products form a perfect gas, and $a$, $b$, $c$, $d$, $e$, $f$, $X$ are the number of moles of $\text{CO}_2$, $\text{CO}$, $\text{H}_2\text{O}$, $\text{H}_2\text{CH}_2$ and $\text{C}$, we have.

\[
\frac{\delta Y}{\delta \delta} = K_1
\]

\[
\frac{\delta^a}{\delta e} = K_2 \frac{V}{RT} \exp \left( -\frac{a \gamma b}{V^a} + \frac{c \epsilon d}{V^c} \right) = K_2'
\]

\[
\frac{\delta^b}{\delta e} = K_3 \frac{V}{RT} \exp \left( -\frac{b \gamma b}{V^b} + \frac{e \epsilon d}{V^e} \right) = K_3'
\]

This of course involves the assumption that no nitrogen compounds are formed among the products. In addition we have the following equations, giving conservation of atomic types, namely
These six equations enable the composition to be determined.

A certain value of \( \alpha \) is assumed, and \( \beta \) and \( \gamma \) determined from (87) and (97). This enables \( \delta \) to be found out from (76) as well as (89). These two values should agree. If found from (76) is greater than that from (89), \( \alpha \) may be increased. If it is the other way, \( \alpha \) may be decreased, till both the values of \( \delta \) agree. A fairly accurate solution is obtained this way.

Working for a loading density \( \frac{\rho}{\gamma} = 0.5 \text{ gm.}/\text{cc} \) the following solution was obtained at a particular temperature.

\[
T = 3400 \, ^\circ\text{K} \quad V = 295 \, \text{cc}
\]

\[
\begin{align*}
\frac{n}{V} &= 0.02983 \\
\left(\frac{n}{V}\right)^2 &= 0.000898
\end{align*}
\]

\[
62.92\left(\frac{n}{V}\right) = 1.077 = A \text{ (say)} \quad 1048\left(\frac{n}{V}\right)^2 = 0.932 = B \text{ (say)}
\]

\[
\begin{align*}
A + B &= 2.009 \\
\epsilon^{-2} &= 0.090 \\
e^{-2} &= 0.060265
\end{align*}
\]

\[
\frac{V}{RT} = \frac{295}{82.00 \times 3400} = 1.0573 \times 10^{-3}
\]

Connection Factor = \( 6.371 \times 10^{-5} \)

\[
\begin{align*}
\frac{\delta Y}{\delta} &= 0.455 \\
\frac{\delta^2 \epsilon}{\delta} &= 3.207 \times 10^4 \times 6.371 \times 10^{-5} = 2.043 \\
\frac{\delta^2 \epsilon}{\alpha} &= 1.167 \times 10^7 \times 6.371 = 106.41
\end{align*}
\]

Composition obtained,

\[
\begin{align*}
\alpha &= 0.244 \quad \theta = 5.095 \\
\delta &= 1.030 \quad \epsilon = 0.523 \\
\gamma &= 1.138 \quad \nu = 1.500 \text{ (Nitrogen)} \\
\alpha &= 0.205
\end{align*}
\]
The value of the energy of these products with respect to its value at room temperature, is given by,

\[ E = 223.86 \text{ Kcal.} \]

This form of the state equation does not give rise to any interaction term in the energy, and hence this temperature dependent part is the total energy of the products. The heat of the reaction \( H \) is given by,

\[ H = a\text{HF}_\text{CO}_2 + \beta\text{HF}_\text{CO} + \gamma\text{HF}_\text{H}_2\text{O} + \epsilon\text{HF}_\text{CH}_4 - \text{HF}_\text{TNT} \]

where \( \text{HF}_\text{CO}_2 \) etc. represents the heat of the formation of carbon dioxide etc. Making use of the following table we have,

Table 7

<table>
<thead>
<tr>
<th>Substance</th>
<th>CO(_2)</th>
<th>CO</th>
<th>H(_2)O</th>
<th>CH(_4)</th>
<th>TNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of formation</td>
<td>94.555</td>
<td>27.545</td>
<td>60.000</td>
<td>17.889</td>
<td>13.0</td>
</tr>
</tbody>
</table>

\[ H = 184.79 \text{ Kcals.} \]

\[ 2(E-H) = 78.14 \text{ '11} \]

Also

\[ p = 0.520 \text{ Kcal/cc.} \]

\[ V_o-V = 150.27 \text{ cc} \]

\[ V = 295 + 5.4 \times 1.138 = 301.45 \text{ cc} \]

\[ V_o = 451.42 \text{ cc} \]

\[ \rho = 0.503 \text{ gm./cc.} \]

Proceeding along these lines the following sets of values were obtained.
The value of $p$ and $v$ at the CJ point is

\[ p = 0.41 \text{ Kcal/cc}, \]

\[ V = 330.5 \text{ cc} \]

giving

\[ D_{\text{cal.}} = 3547 \text{ m./sec.} \]

\[ D_{\text{obs.}} = 3200 \text{ m./sec.} \]

Similar calculations for a loading density of 1.57 gms. gave

\[ D_{\text{cal.}} = 6400 \text{ m./sec.} \]

as compared to the experimental value of

\[ 6900 \text{ m./sec.} \]

These results were obtained by the values of $b$ and $c$, as obtained from the data on PETN, and assuming them to be constant. This however is not the case, for due to the wide change in the composition and the number of gm. moles, the values of $b$ and $c$ do not remain constant. In order to find improved values, of $b$ and $c$ the value of the third virial coefficient for CH$_4$ is not available in the tables. A few trials were made and with improved values $b$ and $c$ found from the composition at the CJ point, and an arbitrarily assigned value of $436(\text{cc/mole})^2$ for the third virial coefficient for methane, calculations were repeated and following results were obtained.
Table 9

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Loading density ( \rho ) gm/cc</th>
<th>Pressure ( p \times 10^{10} ) dynes/cm²</th>
<th>Temperature ( T ) *K</th>
<th>D cal. m./sec.</th>
<th>D obs. m./sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroglycerine</td>
<td>1.62</td>
<td>19.10</td>
<td>5200</td>
<td>7360</td>
<td>7500±500</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>1.67</td>
<td>3200</td>
<td>3425</td>
<td>3200</td>
</tr>
<tr>
<td>TNT</td>
<td>1.55</td>
<td>14.6</td>
<td>4200</td>
<td>6667</td>
<td>6000</td>
</tr>
</tbody>
</table>

4. DISCUSSION

The approach adopted here is in principle similar to that of Cooks, who starting with the Abels equation of state, determined the covolume, from the data on various explosives, regarding it, as a function of the loading density. The pressure and temperature obtained therefore agree very closely with his results for corresponding loading densities. The calculations in this attempt, however reveal, as shown by Table 9, that the agreement of the detonation velocity with the experimentally observed value is better for the oxygen balanced explosives Nitroglycerine, than for TNT. Another feature of the result is that for higher pressure regions, the calculated value is less than the experimental one, while for low pressures it is the reverse. The procedure followed in the present case has been of finding \( \psi \), as a function of \( \frac{V}{n} \), from oxygen balanced explosives, and regarding it the same function \( \frac{V}{n} \) for other explosive. The quantity \( V/n \) is connected with \( \frac{\Delta u_c}{\Delta H} \), \( \mu_n \) being the chemical potential of the mixture. The method consisting in finding \( \psi \) from explosive data, carries with it the assumption, as mentioned earlier, of a common value of the chemical potential \( \mu_1 \) for the mixture. There is a reason to believe that this value of \( \mu_1 \) and hence of \( \frac{V}{n} \) may not be the same for \( O_2 \) balanced and negative
explosive, for they do not form exactly similar mixtures, and $\psi$ may be a different function $\frac{S}{n}$ in the later case. The agreement may therefore be considered satisfactory.

The value of the third coefficient for methane, can only be regarded an approximate one, giving only a correct order of magnitude for it has been determined on the basic of the composition found with a common value of $p^*$ in the first instance.