

AN EQUATION OF STATE FOR THE DETONATION OF CONDENSED EXPLOSIVES

by M. P. MURGAI, *Defence Science Organization, Ministry of Defence,
New Delhi*

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1. INTRODUCTION

Hirschfelder and Roseveare (1939) 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 (1939), Happel (1906) 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 (1948) applied this equation of state to the detonation of condensed explosives. Recently there have been some attempts by De Boer and Michels (1941) and Montroll and Mayer (1941), to evaluate the cluster integral, relating to the third virial coefficient, directly in terms of the Lennard-Jones spherical potential.

Corner (1946) 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.

2. FUNDAMENTAL EQUATIONS

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

$$\frac{pv}{nRT} = (h + \psi) \quad \dots \quad (1)$$

where h is the factor known from Corner's results, and ψ is to be determined.

$$h = 1 + \frac{nb}{v} + \frac{n^2c}{v^2}$$

b and c being the coefficients for the mixture and $nb = \sum n_i B_i$, $nc = \sum n_i c_i B_i$ and C_i being those for the individual gases. Determining the composition from water gas equilibrium, at 4000°K., and making use of Corner's tables,

$$nb = 3.4603 \times 10^2$$

$$n^2c = 2.6986 \times 10^4$$

by the linear law of combination.

From (1)

$$\psi = \frac{pv}{nRT} - h.$$

Differentiating this w.r.t. v we have

$$\frac{d\psi}{dv} = \frac{1}{nRT} \left[v \left(\frac{dp}{dv} \right)_H + p \right] - \frac{pv}{nRT^2} \left(\frac{dT}{dv} \right)_H + \frac{g}{v}$$

where

$$g = \frac{nb}{v} + \frac{2n^2c}{v^2} \dots \dots \dots \quad (2)$$

The well known Rankine Hugoniot equation in detonation is,

$$E - H = \frac{1}{2}p(v_0 - v) \dots \dots \dots \quad (3)$$

where E is the energy of the product gases, w.r.t. their value at room temperature, per gm. mole of the explosive, H the heat of the reaction, v_0 and v the original and the final volume (per gm. mole). For oxygen positive explosive PETN ($E - H$) is linear over a wide range of temperature, and may be expressed as

$$E - H = \alpha T - \beta$$

$$\alpha = .1151 \text{ kil. cal./degree/gm. mole of PETN}$$

$$\beta = 528.05 \text{ kil. cal./gm. mole of PETN} \dots \dots \dots \quad (4)$$

α, β being constants having dimensions of sp. heat and energy respectively. With the introduction of (4), (3) becomes

$$2(\alpha T - \beta) = p(v_0 - v)$$

or

$$T = \frac{p}{2\alpha} (v_0 - v) + \beta/\alpha. \dots \dots \dots \quad (5)$$

Differentiating (5) we have,

$$\left(\frac{dT}{dv} \right)_H = \frac{1}{2\alpha} (v_0 - v) \left(\frac{dp}{dv} \right)_H - \frac{p}{2\alpha} \dots \dots \dots \quad (6)$$

Substituting from (6) and (1), (2) is given by,

$$\frac{d\psi}{dv} = \frac{2\alpha \left[v \left(\frac{dp}{dv} \right)_H + p \right]}{nR [p(v_0 - v) + 2\beta]} - \frac{(h + \psi) \left[(v_0 - v) \left(\frac{dp}{dv} \right)_H - p \right]}{p(v_0 - v) + 2\beta} + g/v. \dots \quad (7)$$

The Chapman Jouguet condition, fixing unique value of the detonation velocity, is expressed by the relation

$$\left(\frac{dp}{dv}\right)_H = -\frac{p}{v_0 - v} \dots \dots \dots (8)$$

This enables $\left(\frac{dp}{dv}\right)_H$ from (7) to be eliminated leading to the equation,

$$\frac{d\psi}{dv} = \frac{2\alpha \left[-\frac{pv}{v_0 - v} + p \right]}{nR[p(v_0 - v) + 2\beta]} + \frac{2p(h + \psi)}{p(v_0 - v) + 2\beta} + g/v \dots \dots (9)$$

The experimentally determined quantity is the detonation velocity. Before the equation expressing $\frac{d\psi}{dv}$ can be usefully employed, the pressure p has to be eliminated. The relation between pressure and the detonation velocity is expressed by

$$D^2 = \frac{p}{(v_0 - v)m} v_0^2 \dots \dots \dots (10)$$

m being the molecular weight of the explosive. Putting the value of p from (10) and defining the following dimensionless variables, namely

$$\xi = \frac{v}{v_0}; \quad \eta = \frac{\beta}{mD^2}; \quad \phi = \frac{nR}{\alpha}$$

(9) reduces to

$$v_0 \frac{d\psi}{dv} = \frac{2(1 - 2\xi)}{\phi[(1 - \xi)^2 + 2\eta]} + \frac{2(h + \psi)(1 - \xi)}{[(1 - \xi)^2 + 2\eta]} + g/\xi = \Theta(\xi\eta\phi \dots) \dots (11)$$

Now

$$\begin{aligned} \frac{d\psi}{d\xi} &= \frac{d\psi}{dv} \cdot \frac{dv}{d\xi} \\ \frac{dv}{d\xi} &= v_0 + \xi \frac{dv_0}{d\xi} \end{aligned}$$

With this (11) becomes

$$\frac{d\psi}{d\xi} = \Theta \left[1 + \frac{\xi}{v_0} \frac{dv_0}{d\xi} \right] \dots \dots \dots (12)$$

Elimination of T and p between (1), (5) and (10) provides another relation in terms of the dimensionless variables, namely

$$\phi(h + \psi)[(1 - \xi)^2 + 2\eta] + 2\xi(\xi - 1) = 0 \dots \dots \dots (13)$$

The equations (12) and (13) are the two equations giving two relations between ψ and ξ from which v_0 can be eliminated and $\psi(v)$ found out. There is, however, no a priori information available on $v_0(\xi)$ relation to enable (12) to be integrated. In order to proceed towards solution, we put

$$\psi = \frac{n^3 d}{v^3} \quad (n \text{ being} = 11.0) \dots \dots \dots (14)$$

as a first approximation. This changes the differential equation (11) into an ordinary algebraic equation given by

$$2\xi\phi(h + \psi)(\xi - 1) - \phi(g + 3\psi)[(1 - \xi)^2 + 2\eta] + 2\xi(2\xi - 1) = 0 \dots (15)$$

This combined with (13) while giving a ψ vs. v solution, also provides $\eta(\xi)$ and $v_0(\xi)$ relations. This solution is tabulated in Table I.

TABLE I

Loading density ρ_0 gms./c.c.	Volume v_0	Volume v	ξ	η	$d \times 10^{-5}$
.25	1264.8	840.1	.6642	.6649	.968
.50	632.4	441.6	.6983	.4589	.204
.75	421.6	308.3	.7313	.3133	.134
1.00	316.2	238.5	.7543	.2266	.096
1.50	210.8	167.2	.7932	.1209	.075
1.72	183.8	147.3	.8014	.1013	.059

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. The value of this coefficient calculated for non-attracting rigid spheres is equal to $.0893 \times 10^6$ so that it corresponds to about the middle of the above table.

Logarithmic plot of v_0 and ξ as shown in Fig. 1 gives a straight line which gives the following relation between v_0 and ξ .

$$v_0 = 16.38 \xi^{-10.417} \quad \dots \quad (16)$$

Making use of this approximation (12) reduces to

$$\frac{d\psi}{d\xi} = -9.417 \left[\frac{2(1-2\xi)}{\phi[(1-\xi)^2+2\eta]} + \frac{2(h+\psi)(1-\xi)}{[(1-\xi)^2+2\eta]} + g/\xi \right] \quad \dots \quad (17)$$

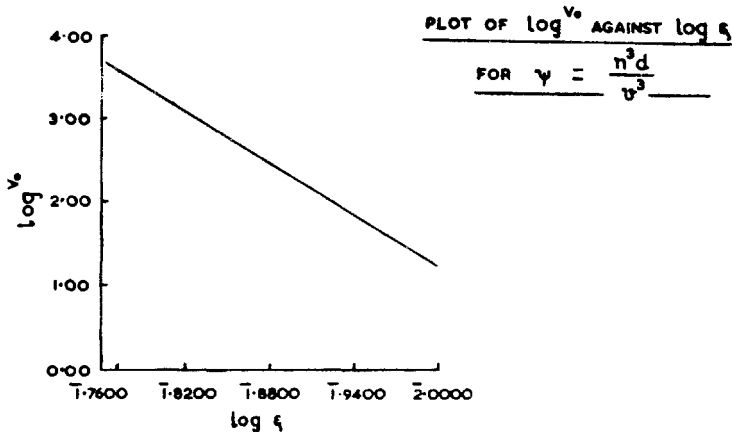


FIG. 1

Figure (2) below gives the relation between η and ξ extrapolated to low densities. Numerical integration of (17) with the help of (16) and Fig. 2 leads to a $\psi(\xi)$

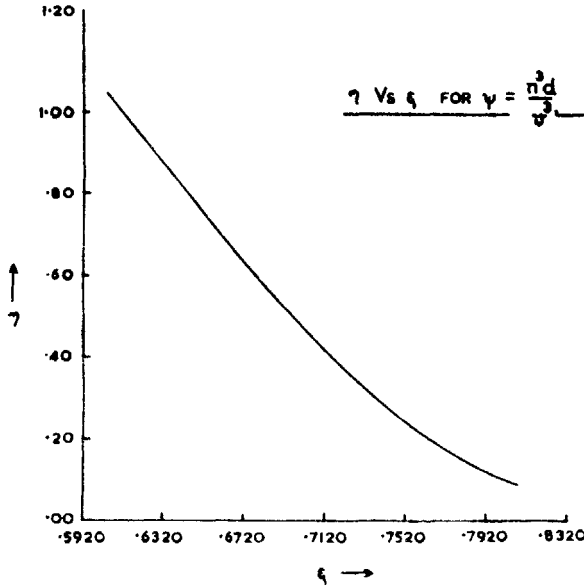


FIG. 2

relation of a better approximation. The initial conditions chosen were $\psi = 0$ for $\rho_0 = .1$ gm./c.c. Combining it with (13) the final $\psi(v)$ relation can be mapped out. It is graphed in Fig. 3. The other parameters pressure and temperature

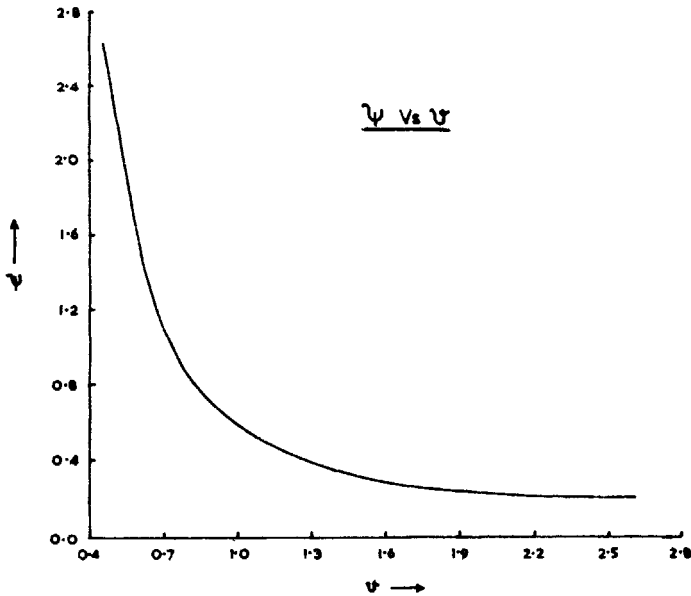


FIG 3.

for PETN can now be easily found out by virtue of the relations (1) and (10). The results are given in Table 2.

TABLE 2

Loading density ρ_0 gms./c.c.	Volume c.c./gm.	ψ	Pressure $p \times 10^{-10}$ dynes/cm. ²	Temperature $T^\circ\text{K.}$
.25	2.616	.2144	.908	4917
.50	1.341	.3388	2.504	5045
.75	.934	.6564	5.001	5155
1.00	.724	1.012	8.514	5277
1.50	.514	2.278	19.85	5491
1.72	.453	2.603	26.22	5599

Leaving aside the value for $\rho_0 = .25$ gms./c.c., ψ can be represented by

$$\psi = \frac{5.74 \times 10^4}{v^2} \dots \dots \dots (18)$$

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 ψ thus found can be switched over to other explosives. This will entail the assumption that ψ remains the same function of $\frac{v}{n}$ from one explosive to another. So we have

$$\psi = 475.5 \left(\frac{n}{v}\right)^2 \dots \dots \dots (19)$$

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

$$\frac{pv}{nRT} = 1 + 31.46 \left(\frac{n}{v}\right) + 698.5 \left(\frac{n}{v}\right)^2 \dots \dots \dots (20)$$

It is interesting to note that ψ 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 1 would reveal that the variation in d is about the same as the variation in v (except for the value for $\rho_0 = .25$ gms./c.c.) 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.

3. APPLICATION TO OTHER EXPLOSIVES

Having constructed the equation of state it can now be applied to the investigation of other explosives.

For oxygen positive or oxygen balanced explosives the value of the detonation velocity can be found out just by the application of equations (3), (8) and (10) mentioned above along with the equation (20). For the former type of explosives the composition of the products can be fairly accurately put, straight from the constitution of the explosives without any resort to chemical equilibria. For the later type it is mainly determined by the water gas equilibrium. In view of the assumptions embodied in the state equation (that of the same field of force for all species in the mixture of products) the correction for the equilibrium constant K reduces to unity, and the products therefore can be determined by the value of K for ideal gas condition. On the other hand, the products of oxygen negative explosives do not get determined unless some equilibria in addition to the water gas are considered. That needs a correction to the equilibrium constant for which the fugacity p_i^* given by the integral

$$RT \ln p_i^* = \int_v^\infty \left[\left(\frac{\delta p}{\delta n_i} \right)_{vTn_j} - \frac{RT}{v} \right] dv - RT \ln \frac{v}{n_i RT} \dots \dots (21)$$

has to be calculated. Solving this with the help of equation (20) we have

$$p_i^* = \frac{n_i RT}{v} \exp \left[62.92 \left(\frac{n}{v} \right) + 1048 \left(\frac{n}{v} \right)^2 \right]. \dots \dots (22)$$

The equilibrium constant for a reaction like

$$a_i + a_j = a_{ij}$$

is given by

$$K \times \frac{\left(\frac{p_i^*}{p_i} \right) \times \left(\frac{p_j^*}{p_j} \right) p}{\left(\frac{p_{ij}^*}{p_{ij}} \right) n} = \frac{n_{ij}}{n_i n_j}.$$

We have

$$\frac{p_i^*}{p_i} = \frac{p_j^*}{p_j} = \frac{p_{ij}^*}{p_{ij}} = \frac{p^*}{p}$$

(same field of force for all gases), therefore

$$\frac{n_{ij}}{n_i n_j} = K \frac{n}{p^*}.$$

In a previous publication the author (1953) has explained the procedure needed for the solution of the problem of oxygen negative explosives, once p^* has been found out. Due to the wide variation in composition, number of gm. moles, etc., with pressure and temperature, the same value of b and c cannot hold good for the entire range of loading density in this case. Solution with the above state equation, however, provides a data for the next approximation to be carried out with improved values of b and c , which can be found out from the tables. In doing so the value of the third virial coefficient for methane, however, is not available. Adjusting the value of c arbitrarily, for one loading density, a value of 436 (c.c./mole)² for

methane was found to give good fit. With this value the results for the other loading density were calculated. The results are given in Table 3.

TABLE 3

Explosive	Loading density ρ_0 gms./c.c.	Pressure $p \times 10^{-10}$ dynes/cm. ²	Temperature $T^\circ\text{K.}$	$D_{\text{cal.}}$ met./sec.	$D_{\text{obs.}}$ met./sec.
Nitroglycerine ..	1.62	19.10	5200	7360	7500 \pm 500
TNT50	1.67	3200	3425	3200
	1.55	14.6	4280	6667	6800

4. DISCUSSION

The approach adopted here is in principle similar to that of Cooks (1947), who starting with the Abel's 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 3, 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 ψ as a function of $\frac{v}{n}$ from oxygen balanced explosive and regarding it the same function $\frac{v}{n}$ for other explosives. This quantity is connected with

$$\left(\frac{\partial \mu}{\partial p}\right)_{T, n_j, \dots}$$

μ being the chemical potential of the mixture. The method consisting in finding ψ from explosive data carries with it the assumption as mentioned earlier of a common value of the chemical potential μ for the mixture. There is a reason to believe that this value of μ and hence of $\frac{v}{n}$ may not be the same for O_2 -balanced and O_2 -negative explosive, for they do not form exactly similar mixtures, and ψ may be a different function $\frac{v}{n}$ in the later case. The agreement obtained 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 basis of the composition found with a common value of p^* in the first instance.

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ABSTRACT

The range of validity of Corner's equation of state, hitherto applied by him to the investigation of the properties of propellants, has been extended to higher pressure regions by the application of the hydrodynamic theory of detonation and the results applied to the determination of the detonation parameters of O_2 -balanced and O_2 -negative explosives. An estimate of the third virial coefficient of the methane gas has been made.

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