UNCLASSIFIED

AD 116872

Armed Services Technical Information Agency

Reproduced by

DOCUMENT SERVICE CENTER

KNOTT BUILDING, DAYTON, 2, OHIO

UNCLASSIFIED

NAVORD REPORT 1508
FIRST REVISION

ANALYSIS OF EXPERIMENTAL DATA ON DETONATION VELOCITIES

1 NOVEMBER 1956

U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

NAVORD Report 1508

ANALYSIS OF EXPERIMENTAL DATA ON DETONATION VELOCITIES

by:

E. A. Christian and H. G. Snay

ABSTRACT: The Kistiakowsky-Wilson equation of state appears to be satisfactory if the proper covolume factors are used. A set of covolume factors is determined by analysis of the measured detonation velocity vs. loading density curves for 21 explosives. Two arbitrary decomposition equations are considered, and any solid products formed assumed to be incompressible. There is some indication that carbon may be in the diamond form in some cases. The proposed new covolume factors are:

CO_2	525
CO	313
H_2O	285
N_2	334
H_2	60

U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

This report is part of a comprehensive project which deals with the calculation of shockwave and detonation parameters from the chemical composition of the explosive.

The data and conclusions presented in this report are for information only. The authors believe that their results are substantially correct, but realize that there may be changes as new data become available. This work was performed under Task NOL-Re2c-3-1-51.

This revision supersedes NAVORD Report 1508, issued 1 February, 1951.

W. W. WILBOURNE
Captain, USN
Commander

JE Ablard
J. E. ABLARD
By direction

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SYMBOLS

A, B	Components of $\bar{C}_v \cdot n_g$
c	Sound velocity
$\bar{C}_v$	Average specific heat of the ideal gas at constant volume between room temperature and T
D	Detonation velocity
HF	Heat of formation
HFE	Heat of formation of the explosive
HFP	Heat of formation of the decomposition products
h	Covolume factor per weight unit gas $h = k/M_g$
I	I-function
k	Empirical covolume constant of Wilson-Kistiakowsky equation
$\bar{k}$	Covolume factor referring to one mole of gas, $\bar{k} = k/n_g$
m	Molecular weight
M_o	Weight of explosive considered
n	Number of moles
n_g	Number of gaseous moles in M_o
p	Pressure
Q	Heat of detonation
R	Gas constant
T	Temperature
U	Particle velocity
v	Specific volume
x	Defined in equations
η	Weight fraction of the solid products
α	Defined in equations
β	Defined in equations
ρ	Density

SUBSCRIPTS

B	Refers to fictitious state
D	Refers to Chapman-Jouguet point
g	Refers to gaseous components
i	i-th product
m	Refers to mixture
o	Refers to loading conditions
s	Refers to solid products

I INTRODUCTION

1. Nature of Problem

For thermodynamic calculations of explosion phenomena, an equation of state applicable to pressures of the order of 100 kilobars and temperatures of the order of 3000°K must be known. Information on such gas states can be obtained by use of the hydrodynamic theory of the detonation process, if experimentally measured detonation velocities as a function of the loading density of the explosive are known. For an ideal gas, the detonation velocity is independent of the density. Detonation velocities of solid explosives show a definite increase with increasing loading density, due to the imperfect behavior of the explosion gases. Such measurements, therefore, provide a very suitable means of finding the deviations of the explosion gases from ideal-gas behavior.

A. Equation of State. H. Jones, who gave a very elegant analysis of this problem 1/*, has shown that it is not possible to determine a complete equation of state in this way. However, once a form of the equation is established, the D - ρ_0 relationship is sufficient for the quantitative determination of its empirical parameters. Thus a p-v-T relationship can be determined. The accuracy of such an equation of state depends primarily on the initially assumed form. Jones' analysis, however, shows that the p-v relationship is rather insensitive to this form. Therefore, the experimental proof of the question of whether or not an assumed form of the equation of state is appropriate should be obtained by measurements of the detonation temperature. Since such measurements have not been made to date we must be reconciled to the other possible attack - namely, to use the best available form of the equation of state. In this paper the form of the Kistiakowsky-Wilson equation of state 2/ has been chosen; it is considered to be the best we have at the present.

This equation of state has been successfully used in many theoretical investigations of detonation and shockwave phenomena. Brinkley and Wilson 3,4/ used it in their calculations of detonation velocities. The results, while in satisfactory

---

* Numbers so indicated refer to the list of references at the end of this report.

agreement with measured values in the majority of cases, were in rather poor agreement for two explosives, hydrazine nitrate and nitroguanidine. These discrepancies could be attributed either to inadequacy of the Kistiakowsky-Wilson equation of state, especially its empirical factors α and β (cf. Section 7), or to the values of the covolume factors used in those calculations.

This paper represents a study of this question. It was found that the Kistiakowsky-Wilson equation of state does not lead to any contradictions with experiments and that the discrepancies mentioned above were due to the covolume factors. A new set of covolume factors which give good agreement for all the considered experimental data has been determined.

B. Compressibility of Solid Products. Another problem studied concerned the influence of the compressibility of the solid decomposition products on the detonation process. This study gave some information about density and state of the solid carbon formed as a reaction product by oxygen-deficient explosives.

2. Decomposition Equation

Throughout the investigation discussed here, the assumption of an arbitrary decomposition equation was used. Two such equations were considered; the "H_2O arbitrary", suggested by Brinkley and Wilson 3/, and the "CO arbitrary", used by Wilson and Kistiakowsky 2/. In both of these decomposition equations, components which occur in small amounts, such as CH_4, NH_3, HCN, NO, OH, and frequently CO_2 and H_2, are neglected. Because of its simplicity, an arbitrary decomposition equation is particularly useful to avoid laborious computations.

Such simplified calculations can serve as a basis for further studies which consider equilibrium conditions. They provide approximate parameters for the equation of state, which can be used in the first step of the iteration process necessary for determining the equilibrium composition. Although the use of equilibrium calculations may be indicated for aluminized explosives the consideration of the two arbitrary decomposition equations has provided a study of both extremes which might be encountered as far as the most important equilibrium is concerned - namely, the "water-gas" equilibrium*. Equilibria concerning NH_3 or CH_4 are, of course, not covered.

II SUMMARY OF RESULTS

In order to determine the empirical parameters of the equation of state, the detonation velocities were calculated by methods described in Section 8, and the theoretical values so obtained were compared with experiment. The calculations were repeated with different values until the calculated and experimental results were in satisfactory agreement.

3. The Parameters α and β of the Kistiakowsky-Wilson Equation of State

The Kistiakowsky-Wilson equation of state has three arbitrary parameters, viz, α , β and k. α and β are assumed to be independent of the composition of the gas, whereas k, the covolume factor, may vary with the composition. The values for α and β proposed by Kistiakowsky and Wilson are

$$\alpha = 0.25$$
$$\beta = 0.30$$

With the use of these values of α and β, and with k alone varying, it was found that in almost all cases the calculated curves reproduced quite well the measured D - ρ_0 relationship. The final values of k determined in this way appear to be consistent for different explosives. This evidence indicates strongly that the Kistiakowsky-Wilson equation of state with its same empirical parameters α and β is appropriate.

The desirability of retaining the Kistiakowsky-Wilson equation in its original form is apparent. This equation has been used in many previous investigations with great success, and many tables based on it are available. The satisfactory over-all results shown in Figs 1 to 20 offer further evidence that no change of this equation of state is justified, as long as there is no better experimental evidence available than D - ρ_0 data. To be sure, the Kistiakowsky-Wilson equation is

---

* $H_2 + CO_2 = H_2O + CO$

$2CO = CO_2 + C$

more or less empirical in character, and it is not quite clear whether its form is actually the one best suited for this purpose. In any case, it does not seem desirable to augment the vast number of existing empirical equations of state until more basic evidence on this problem is gathered, either theoretically with regard to the form of the equation, or experimentally by reliable temperature measurements for the Chapman-Jouguet state. Such results will prove whether or not the Kistiakowsky-Wilson equation of state is adequate. The investigations of this paper show only that no serious contradictions with available experimental evidence are encountered if this equation of state is properly used for problems of detonation phenomena.

4. Covolume Factors

The determination of covolume factors (cf. Equation (10)) was entirely independent for each of the arbitrary decomposition equations, though the procedures followed were the same. For a given decomposition equation, a $k_{observed}$ was chosen for each explosive. The value of $k_{obs.}$ is that total covolume factor for the gaseous decomposition products which gave best average agreement between calculated and experimental values of D over the density range of the explosive. The values of $k_{obs.}$ are shown in Tables IA and IB (column 20).

The assumption was made that k is an additive function of values characteristic of the different gaseous product molecules H_2O, CO, N_2, CO_2 and H_2:

$$k = n_{CO_2} k_{CO_2} + n_{CO} k_{CO} + n_{H_2O} k_{H_2O} + \dots \quad (1)$$

Each set of decomposition products, with its corresponding $k_{obs.}$, was represented in such a linear equation. Thus for each explosive there were two such equations, one based on each of the arbitrary decomposition equations. The set of covolume equations (1) for the same arbitrary decomposition provided a system of about 20 linear equations from which the species covolume factors, k_{CO_2}, k_{CO}, etc. were found by the method of least squares.

The influence of lead azide (which has only N_2 as a gaseous decomposition product) upon the least squares calculations was so great that sets of species covolume factors were calculated both with and without its inclusion. The four sets of k_1 found from least squares are:

H_2O Decomp. Equation	k_{CO_2}	k_{CO}	k_{H_2O}	k_{N_2}	k_{H_2}
I. Omitting $Pb(N_3)_2$	527	314	249	389	---
II. Including $Pb(N_3)_2$	521	314	287	334	---
CO Decomp. Equation					
III. Omitting $Pb(N_3)_2$	534	314	239	400	10
IV. Including $Pb(N_3)_2$	531	313	284	334	60

It is interesting that the k_i's from the two different decomposition equations are virtually the same, although all of the factors involved in the calculations are different for the two treatments. (cf. n_g, $k_{obs.}$, Q, etc., Tables IA and IB.)

The total covolume factors ($\Sigma n_i k_i$) calculated for each explosive from these four sets of species covolumes are shown in Table III, columns (2), (4), (7) and (9). The agreement between particular values of $\Sigma n_i k_i$ and $k_{obs.}$ is indicated in columns (3), (5), (8) and (10), Table III, where $\delta = k_{obs.} - \Sigma n_i k_i$. The agreement between $\Sigma n_i k_i$ and $k_{obs.}$ is quite good in general, which is remarkable, because the covolume of a gaseous mixture is not the sum of the individual covolumes of the components. Table III shows, however, that this is a good approximation in the cases considered here. Aside from lead azide the greatest percentage discrepancies in k occur for Fivonite (for which there is some uncertainty in the heat of formation; see Section 9) and picric acid. For Fivonite, however, the differences in detonation velocities calculated with the various k's are less than 5%.

In consideration of the over-all agreement of any one group of $\Sigma n_i k_i$ values with the corresponding values of $k_{obs.}$, there is no indication that any one set of the k_i values is notably better than another for the explosives considered. The discussion in Section 10 points out, however, that due to the peculiar distribution of the explosives when gaseous decomposition products are plotted on a percentage basis, the inclusion of an explosive having a predominance of H_2O or N_2 in its products is quite important. Thus it is felt that the species covolume factors in which lead azide was included are the more nearly correct ones.

In addition to the total covolumes k_{obs}, two average values of covolume are shown in Tables IA and IB, the covolume factor per weight unit gas:

$$h = k_{obs.}/M_g \qquad (2)$$

and the average covolume factor of the gaseous mixture referring to one mole of gas

$$\bar{k} = k_{obs.}/n_g \qquad (3)$$

The values of h for the CO decomposition equation are the same as, or slightly lower than, those for the H_2O decomposition equation. The latter values are for the most part near 12.5. Hydrazine nitrate, which forms no CO, has the highest value: $h = 14.0$

For those explosives whose product gases are quite different for the two arbitrary decompositions, the values of $\bar{k}$ for the CO decomposition are consistently much lower than those for the H_2O decomposition. In the H_2O group, all of the $\bar{k}$ values fall surprisingly near 310, if the high $\bar{k}$ values of explosives forming CO_2 are omitted. The CO $\bar{k}$ values show a much greater variation.

5. Solid Products*

Theoretical considerations 6/ show that two factors are important in the influence of the solids: the "adiabatic compressibility" of the solids, and their actual volume. If the adiabatic compressibility of the solids is assumed to be negligibly small in comparison with that of the gases, the case is called that of incompressibile solids. The assumption that solid products are incompressible relative to the gases does not remove the possibility that their actual volume may vary.

According to theory, the lowest values of detonation velocity are obtained when the solids are assumed to be incompressible, everything else - including the actual

---

* The discussion of solid products applies to calculations based on the assumption of the H_2O arbitrary decomposition equation. With the CO arbitrary decomposition equation, only TNT and Picratol form solid carbon-in negligibly small amounts.

volume of the solids - being held constant. This treatment seems appropriate for TNT, since calculated detonation velocities were too high at high loading densities (see Fig. 25), when the solid carbon was assumed to be in the graphite form. Consideration of finite relative adiabatic compressibility of the solids would increase the theoretical detonation velocity and thus increase the deviation from experimental values. The same was found to be true of all other explosives where solid carbon occurs in the decomposition products. It can be concluded, therefore, that the assumption of adiabatic incompressibility of solid carbon (in comparison with that of the gases) is reasonable. This result was not necessarily to be expected, since the adiabatic compressibility of carbon at normal conditions is similar in order of magnitude to that of the gases at Chapman-Jouguet conditions.

The other factor involved is the actual specific volume of the solid products. Since the effects of high pressures and high temperatures tend to be compensatory, the assumption of normal density does not seem unreasonable. This magnitude, however, depends not only on the compressibility and thermal expansion of the solid, but also on its crystal structure. Detonation velocity data can provide some information on this problem. With a volume of carbon equal to that of graphite, the theoretical curve gives too high values of D at high loading densities, but satisfactory values at the lower densities. If the carbon is assumed to have the volume of diamond at high density, the volume of graphite at low density, and related volumes at intermediate densities, a surprisingly satisfactory "volume correction" results.

This proposed variation of the specific volume of solid carbon formed in the detonation process is shown in Figure 21 as a function of pressure (solid line). For comparison, the variation of graphite at room temperature 5/, and the value of diamond at room temperature and atmospheric pressure are also shown.

This volume correction, however, should also be a function of the temperature. Since it was not possible to determine such a temperature dependency using results of non-aluminized explosives, the curve of Figure 21 is applicable only for temperatures similar to those of TNT. This volume correction curve for carbon was used for all explosives whose decomposition products contain solid carbon. In all cases, the use of this correction improved the agreement between calculated and experimental values.

6. Consideration of Equilibrium

The possibility was considered that the volume correction of carbon might prove unnecessary when other calculational assumptions are used. For example, since the use of equilibrium calculations involves a variation in the number of gaseous moles (to which the calculated value of D is quite sensitive), it is possible that the carbon correction would not be necessary with such treatment. However, it turned out that the detonation velocities of TNT (calculated with new covolume factors and $y_c = 1$) using the Brinkley equilibrium compositions show the same deviations from experimental as did the arbitrary decomposition equation. Thus, the carbon correction provides better agreement in this case. (See Fig. 25.)

III PROCEDURES OF CALCULATION

Detonation velocities were calculated by the method described in reference 6 and reference 12. For the sake of completeness, a short summary of this method of calculation is given here.

7. Assumptions Used

The calculations are based on the following assumptions:

(A) The Chapman-Jouguet condition exists.
(B) The Kistiakowsky-Wilson equation of state holds for the explosion gases.
(C) The solid products formed are incompressible.

A. The Chapman-Jouguet Condition. It has been established by experiments that the Chapman-Jouguet condition usually applies very well to actual detonation processes, if the grain of the explosive is sufficiently fine and the charge diameter sufficiently large. Since coarse grain and small diameter result in lowered detonation velocities for some explosives, the calculated results should be compared with the highest available experimental values. This was taken into consideration as far as possible in comparing theoretical and experimental values.

In the case of lead azide this was not true. Here the calculated detonation velocities correspond to the lower rather than to the higher measured values (Fig. 20). Lead azide is one of those substances which do not show a diameter effect. In addition, since improved measuring techniques have resulted in lower velocities than the early measurements of OSRD 69, the fitting of the curve to the lower limit seemed to be appropriate. This treatment of lead azide is of very great importance for the determination of the numerical values of species covolume, and is offered only tentatively.

B. The Equation of State. The Kistiakowsky-Wilson equation [2,3] applying to a mixture of different gases and small solid particles is

$$p(1/\rho_m - \eta v_s) = \frac{n_g}{M_o} RT(1 + xe^{\beta x}) \cdot \qquad (4)$$

where

$$x = \frac{k}{M_g} \rho_g T^{-\alpha} \qquad (5)$$

$$= h \rho_g T^{-\alpha} \qquad (6)$$

$$= \frac{\bar{k} n_g \rho_g}{M_g} T^{-\alpha} \qquad (7)$$

and where

$$\rho_g = \frac{1 - \eta}{1/\rho_m - \eta v_s} \qquad (8)$$

$$M_g = (1 - \eta) M_o \qquad (9)$$

The symbols are explained in the list of symbols, in the front of this report. Note that the subscript g refers to the gaseous components, s to the solid components, and m to the whole mixture. M_o is the total weight of the mixture considered. α and β are the empirical constants of the Kistiakowsky-Wilson equation. The values $\alpha = 1/4$ and $\beta = 3/10$ have been used throughout this investigation.

k, the covolume factor, is, according to Kistiakowsky and Wilson:

$$k = \Sigma n_i k_i \qquad (10)$$

where k_i is the individual covolume factor of a gaseous component and n_i is the number of its molecules in M_o weight units of the mixture considered. (For solids, $k_i = 0$, since the Kistiakowsky-Wilson equation of state applies to the gas which occupies the volume left by the solids.)

C. Solid Products. The treatment of the solid products was discussed in Section 5, where it was pointed out that only their actual volume need be considered. Since carbon is the only solid product which occurs in the explosives included here, the relationship

$$v_s = y_c \cdot v_{graphite} \quad , \quad y_c = f(p_D) \qquad (11)$$

was used to designate the specific volume of the solid products, and the y_c vs. p_D curve (Fig. 21) explained in Section 5 was used in the calculations for the H_2O decomposition equation.

8. Equations of Detonation Parameters

In reference 6 the following equation for the detonation velocity is derived, based on the above assumptions:

$$D^2 = \frac{n_g \, T_B}{M_o(1-\eta v_s \rho_o)^2} \quad I_D \, (x_B, \overline{C}_v) \qquad (12)$$

I_D can be read from a diagram as a function of x_B and $\overline{C}_v$. A copy of this diagram (Fig. 22), as well as those of other diagrams (Figs. 23 and 24) which will be mentioned below, is included. The subscript B refers to a fictitious state corresponding to a steady-state explosion of an ideal gas:

$$T_B = \frac{Q}{n_g \overline{C}_v} + 300^\circ K \qquad (13)$$

and

$$x_B = h \, \rho_{go} \, T_B^{-\alpha}$$

$$= h \, \frac{1-\eta}{1/\rho_o - \eta v_s} \, T_B^{-1/4} \qquad (14)$$

ρ_o is the loading density of the explosive, Q is the heat of explosion of M_o weight units of explosive, and $\overline{C}_v$ is the ideal average heat capacity of the mixture between 300°K and the actual detonation temperature, T_D, which can be expressed by

$$\begin{aligned} n_g\bar{C}_v &= A + B\cdot T_D \\ A &= \Sigma n_i A_i \\ B &= \Sigma n_i B_i \end{aligned} \qquad (15)$$

A_i and B_i are the components of the average ideal molar heat capacity at constant volume. The summation must include the solid products here also. In our calculations the values quoted by Brinkley and Wilson 3/ were used.

The detonation temperature T_D can be found from Figure 23 which shows T_D/T_B as a function of x_B and $\bar{C}_v$. Since T_D occurs implicitly in T_B, x_B and $\bar{C}_v$, it must be found by means of an iteration process. This iteration converges very rapidly, however, since the influence of T_D on T_B, x_B and $\bar{C}_v$ is relatively small.

The detonation pressure p_D can be conveniently found from

$$p_D = \frac{n_g}{k}\; T_D^{\;5/4}\; I_2\,(x_D) \qquad (16)$$

where $I_2(x_D)$ is shown in Fig. 24 as a function of x_B and $\bar{C}_v$. If the specific volume of the solids is introduced as a function of the pressure, as in equation (11) and Figure 21, an iteration which includes the calculation of the temperature T_D as well as pressure p_D must be performed.

9. Decomposition Equations

The two arbitrary decomposition equations considered, the "H_2O equation" of Brinkley and Wilson 4/ and the "CO equation" of Kistiakowsky and Wilson 2/, give different decomposition products only for explosives which do not contain sufficient oxygen to completely convert carbon to carbon monoxide and hydrogen to water. When an excess of oxygen is present, the following decomposition is assumed:

$$\text{if} \quad \left(q + \frac{r}{2} \leq s\right) \qquad (17)$$

$$C_qH_rO_sN_t = \tfrac{1}{2}r\ H_2O + (s-q-\tfrac{1}{2}r)CO_2 + (2q-s+\tfrac{1}{2}r)CO + \tfrac{1}{2}tN_2$$

When the explosive does not contain sufficient oxygen to convert both its hydrogen and carbon, the decomposition products obtained with the two equations are quite different, since the names "H_2O" and "CO" for the two equations indicate the product which is assumed to be formed first:

$$\text{if } (q + \frac{r}{2} \geqslant s),$$

H_2O arbitrary decomposition equation:

$$C_qH_rO_sN_t = \tfrac{1}{2}r\ H_2O + (s-\tfrac{1}{2}r)CO + (q-s+\tfrac{1}{2}r)C + \tfrac{1}{2}tN_2 \quad (18)$$

CO arbitrary decomposition equation:

$$C_qH_rO_sN_t = q\ CO + (q-s+\tfrac{1}{2}r)\ H_2 + (s-q)\ H_2O + \tfrac{1}{2}tN_2 \quad (19)$$

In the above equations, the coefficients $\frac{1}{2}r$, $(s-\frac{1}{2}r)$, etc., correspond to the n_i values of equation (15). Since the A_i and B_i for H_2, CO, N_2, etc., are known, (15) can be easily evaluated. The same is true for Q which is found from

$$Q = \Sigma n_i\ HF_i + 0.596\ n_g - HFE \quad (20)$$

HFE is the heat of formation of M_o weight units of the explosive. Table IV shows the values of A_i, B_i and HF_i used.

The heats of formation (HFE) which were used (Table IA, column 16; Table IB, column 17) are those of Schmidt 9/. Additional values of HFE from reference 10 are different from those of Schmidt for several explosives. For Fivonite, DINA, and NENO there is sufficient difference in these HFE values to affect the value of Q, and hence the detonation velocity calculations. With the CO arbitrary decomposition equation, k_{obs} was determined for these three explosives using both values of HFE. The effect upon k is shown below. Since both the k_{obs} values gave an equally good fit with the experimental detonation velocities, there was no indication that either value of HFE was preferable.

	HFE_1 (ref. 9)	$k_{obs.1}$	HFE_2 (ref. 10)	$k_{obs.2}$
Fivonite	153	4500	172.57	4550
DINA	100	3100	77.5	3000
NENO	101.8	4380	132.2	4550

Only for NENO is the difference in $k_{obs.}$ values of any importance in this particular calculation. (A value for NENO of HFE = 110 is also reported by Paterson.) In all three cases, the k_{obs} used in the CO least squares determination of species covolumes was the numerical average of the two values shown above. With the H_2O decomposition equation, only the HFE of Schmidt were used to obtain the $k_{obs.}$ of the least squares calculation.

10. Evaluation of Covolume Factors

As was discussed in Section 4, sets of species covolume factors (k_{CO}, k_{N_2}, etc.) were calculated for four conditions: two arbitrary decomposition equations, each with and without lead azide in the least squares calculations. The species covolumes calculated for the different arbitrary decomposition equations are, for all practical purposes, the same, so that the following discussion is concerned only with the effect of lead azide upon the calculations.

Certainly there is some question as to the applicability of a least squares method of calculation which is so sensitive to a particular one of the twenty equations involved. The reason for this sensitivity is apparent from Figure 26, which is a three-component plot of the decomposition products H_2O, CO and N_2. On Figure 26 are shown the explosives which form only these three product gases, according to the H_2O arbitrary decomposition equation* (traces of O_2 in hydrazine nitrate and nitroguanidine are included with N_2). When lead azide is not included, the distribution of points on Figure 26 is limited to a very narrow range of the H_2O/N_2 ratio.

---

* With the CO decomposition equation, of course, a fourth product gas, H_2, is formed, so that Figures 26 and 27 are necessarily significant only for the H_2O decomposition equation.

Figure 27 shows even more clearly the importance of including any available data on explosives having a higher percentage of N_2 or H_2O in the decomposition products. In Figure 27, the explosives of Figure 26 are represented by their $\bar{k}$ values; lead azide is omitted. The plane indicated by the strings is obtained from Equation (21), which is the result of the least squares calculation:

$$k = 314\, n_{CO} + 249\, n_{H_2O} + 389\, n_{N_2} \tag{21}$$

i.e., the plane represents the total covolumes which would be calculated using the species covolume factors based on the H_2O arbitrary decomposition equation, without lead azide.

For the explosives shown, the scatter of the $\bar{k}$ values around this plane is not at all bad if the grossly enlarged scale is taken into account. Note, however, that the above covolume factor of 389 obtained for N_2 results in extremely poor agreement between calculated and experimental detonation velocities for lead azide, whose $\bar{k}$ is 330. (Since N_2 is the only product gas of lead azide, $\bar{k} = k_{N_2}$.) It is also clear from Figure 27 that this k-plane is "supported" only by a relatively narrow strip of observed values as far as the N_2 - H_2O extension is concerned. Consequently, experimental data from explosives at the extremities of this extension - such as lead azide - are of relatively very great significance in determining the validity of the least squares method of calculation for the species covolumes.

The species covolumes calculated for the CO decomposition equation show the effect of lead azide just as clearly as does Figure 27 for the H_2O equation, though a similar pictorial treatment is not possible. With the CO decomposition products, when a high $\bar{k}$ of 350 for lead azide is introduced into the least squares calculation, the k_i's obtained are as follows: $k_{H_2} = 46$, $k_{N_2} = 353$, $k_{H_2O} = 271$, $k_{CO_2} = 532$ and $k_{CO} = 314$. Comparison of these values with those of Table V (where $\bar{k} = 330$ for lead azide) shows that, whereas the covolumes of CO and CO_2 are not affected, the k_i of H_2 as well as that of H_2O is lowered to compensate for the increase in the value for N_2.

For explosives having an empirical formula similar to most of those considered here, the use of any of the sets of species covolume factors would probably be equally satisfactory (cf. δ columns of Table III). In view of the above considerations, however, it is felt that the averages of the species covolume factors obtained from both decomposition equations, with lead azide included, are reasonably reliable for a fairly wide variety of explosives. The proposed set of "new" species covolume factors, k_i, is shown in Table V below. Also shown are the previously calculated covolume factors of Brinkley and Wilson 3/, and those of MacDougall and Epstein (see Section 11, reference 2).

TABLE V
Covolume Factors

	k_i New	k_i Brinkley - Wilson	k_i MacDougall Epstein
CO_2	525	687	549
CO	313	387	316
H_2O	285	108	241
N_2	334	353	316
H_2	60	153	54

Although the MacDougall-Epstein values, like the "new" values, were obtained by a least squares fit of k's, only the CO arbitrary decomposition equation was considered. The differences in these two sets of k_i are apparently due to the fact that the "new" values are based on a somewhat wider range of explosives, of which nitroguanidine and hydrazine nitrate are of particular significance. Also, for some of the explosives included in both calculations, improved data were availabe and a higher $k_{obs.}$ was used in the present calculations.

The sets of k_i obtained in a strictly empirical fashion differ considerably from the Brinkley-Wilson k_i, which were obtained by successive approximations from initial constants chosen proportional to the high temperature Van der Waals' "b" of Hirschfelder.

IV PRESENTATION OF THE CALCULATED DETONATION PARAMETERS

The results of the calculations are shown in Figs. 1-20. The measured detonation velocity vs. loading density graphs are from reference 7, with the exception of those for hydrazine nitrate and lead azide, which comprise unpublished data of the Detonation Division of the Explosives Research

Department of the Naval Ordnance Laboratory. Additional sources of experimental values, if available, are noted on each figure. For each explosive, the calculated curve for each decomposition equation is shown, and the value of $k_{obs.}$ used in each calculation is noted. Curves representing the experimental values are not included on the graphs.

The explosive compositions, decomposition products predicted by the arbitrary decomposition equation, and all the magnitudes involved in the principal steps of the calculations are listed in Tables IA and IB for the H_2O and CO arbitrary decomposition equations respectively. The entries which are the same for the two equations are so indicated in the tables. The $\bar{k}$ and h values of columns (21) and (22) correspond to the $k_{obs.}$ of column (20). The calculated curves shown on Figures 1-20 correspond to these tabulated h, $\bar{k}$ and $k_{obs.}$ values.

In Tables IIA and IIB (H_2O and CO respectively) the measured D and the calculated values of D, T_D, x_D and p_D (for $k_{obs.}$ of Tables I*) are tabulated for several loading densities. The $D_{exp.}$ values are those listed in reference 7, except for nitroglycerine 8/, lead azide and hydrazine nitrate (see above). Magnitudes which can be found by means of simple computations are not tabulated, e.g.,

$$U = (p_D/\rho_o D) \quad x10^5$$

$$\rho_D = \rho_o/(1-\frac{U}{D})$$

$$c_D = D - U$$

Table III is a compilation of the various values of mixture covolume, $\Sigma n_i k_i$, that are calculated with the different sets of species covolume, k_i (see Section 4). As in Tables I, column (20), the $k_{obs.}$ chosen for best fit is shown for each of the two decomposition equations. The $\Sigma n_i k_i$ from k_i with and without lead azide are listed for each $k_{obs.}$, and the differences $\delta = k_{obs.} - \Sigma n_i k_i$ are tabulated.

---

* For DINA, NENO and Fivonite, where two heats of formation were considered (see Section 9), the calculated values of Table II do not correspond to the $k_{obs.}$ of Table I; the $k_{obs.}$ listed is the average one for the different HFE values.

V AGREEMENT BETWEEN CALCULATED AND EXPERIMENTAL DATA ON DETONATION VELOCITIES

As was discussed above, the calculated detonation velocities which are shown on the curves (Fig. 1-20) and in Tables IIA and IIB are those using the adjusted k_{obs}. A comparison of the experimental and calculated values of D shown in Tables II indicates, in some cases, rather poorer agreement than is evident from the graphs themselves. The experimental values listed in these tables are those from reference 7 which result from a straight line representation of the D - ρ_0 relationship. (Experimental values are listed in both Tables IIA and IIB, for convenient reference.) Although this approximation was sufficient in many instances, in others, such as PETN (Fig. 12), NENO (Fig. 9) and hydrazine nitrate (Fig. 8), it is inadequate. A more accurate judgement of the agreement between calculated curves and experimental values is possible from Figs. 1-20 than from Tables II.

Ideally, the calculated D - ρ_0 curves for the two decomposition equations should be the same. It should be noted again, however, that there was one consideration which was necessary for the H_2O equation and not for the CO; namely, the volume correction for carbon (Section 5). TNT, for which the correction was established, was the only explosive giving solid carbon as a decomposition product with the CO arbitrary equation (the minute quantity predicted for Picratol is neglected) whereas the majority of the explosives have solid carbon with the H_2O arbitrary equation. For TNT, the D - ρ_0 curves were calculated for the CO decomposition with the value for carbon volume of both diamond and graphite. The CO calculated curve, carbon volume of diamond, coincided with the H_2O calculated curve, carbon volume variation as shown in Figure 21. The CO calculated curve with carbon volume of graphite, as shown on Figure 19, is only slightly higher than the H_2O curve.

Aside from the few cases where the two curves are at slightly different levels throughout, there is some indication that the slopes of the calculated curves are slightly different for the different decomposition equations. For several explosives (e.g. Comp. A, Ednatol), the curves actually intersect, the CO curve having the smaller slope. In other cases (Comp. B, Pentolite), the difference is apparent in a slightly lower value at high density for the CO curve. Even when the CO and H_2O calculated curves are slightly different, however, the over-all agreement between experimental and calculated values is not appreciably different for the two treatments.

As Figures 1-20 show, the agreement of the calculated curves with the measured points is actually excellent for the majority of the explosives considered, and is very satisfactory in all cases. For several explosives, e. g., Ednatol, there is an interesting systematic deviation at high loading densities, the calculated curve being consistently higher (but not more than ca. 2.5%) than the measured values. It is not clear whether this is a sort of "diameter effect", or an actual "leveling off" of the D - ρ_0 curve. (Compare, for example, Friedrich's values in Fig. 16 and the diameter effect of hydrazine nitrate, Fig. 8.)

For Pentolite, Comp. B and DINA, the slope of the calculated curve is too steep by a small amount. Such a discrepancy could be attributed to the equation of state, or, more specifically, to the constants α and/or β of the Kistiakowsky-Wilson equation. In many other instances, however, with very similar temperatures, pressures and density ranges, the character of the curve is correctly reproduced.

In view of the small magnitude of such deviations, one can probably attribute these discrepancies to a "scatter". In fact, the over-all agreement is as good as can be expected from such an empirical equation of state, and is felt to be completely satisfactory.

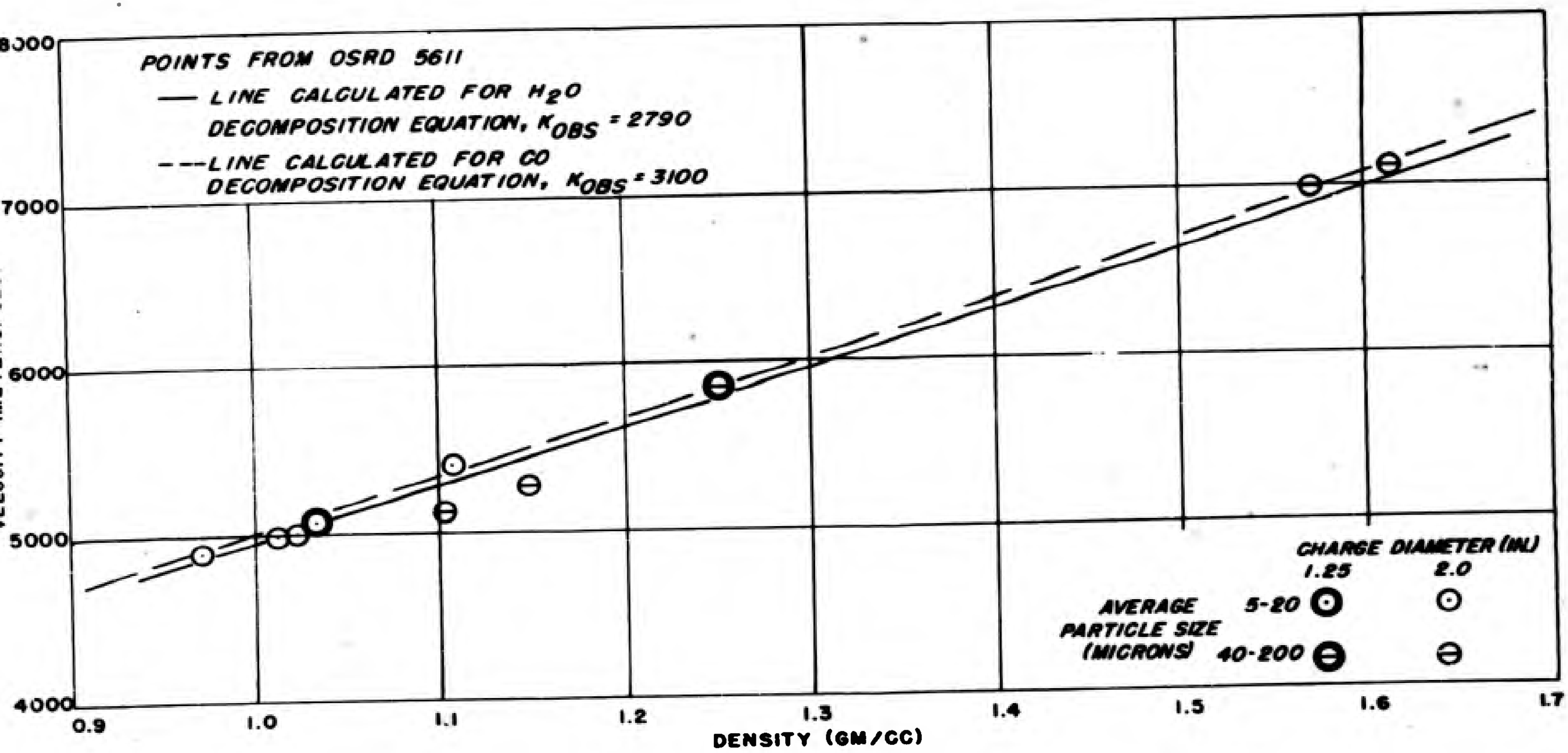


FIG. 1
AMMONIUM PICRATE

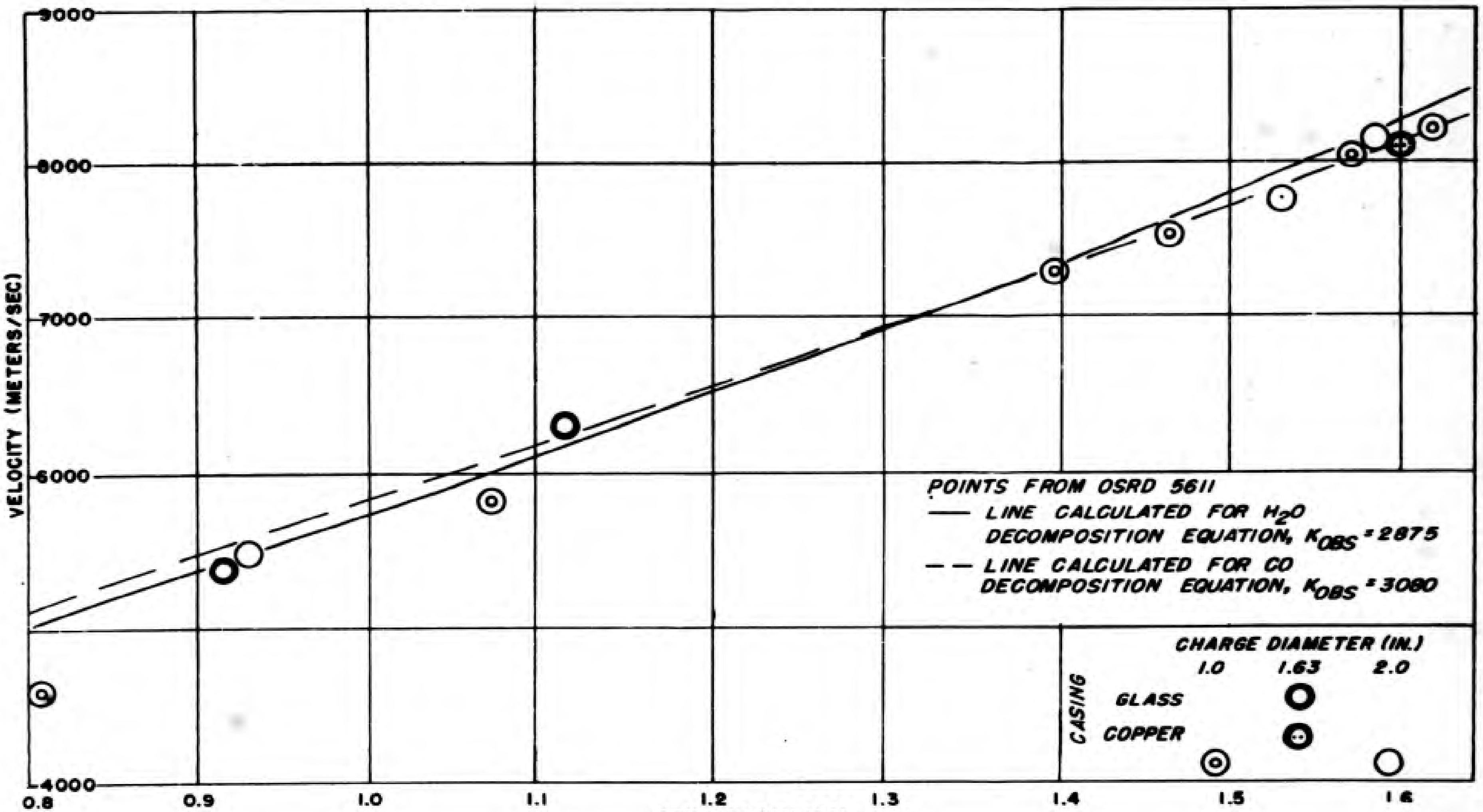


FIG. 2
COMPOSITION A

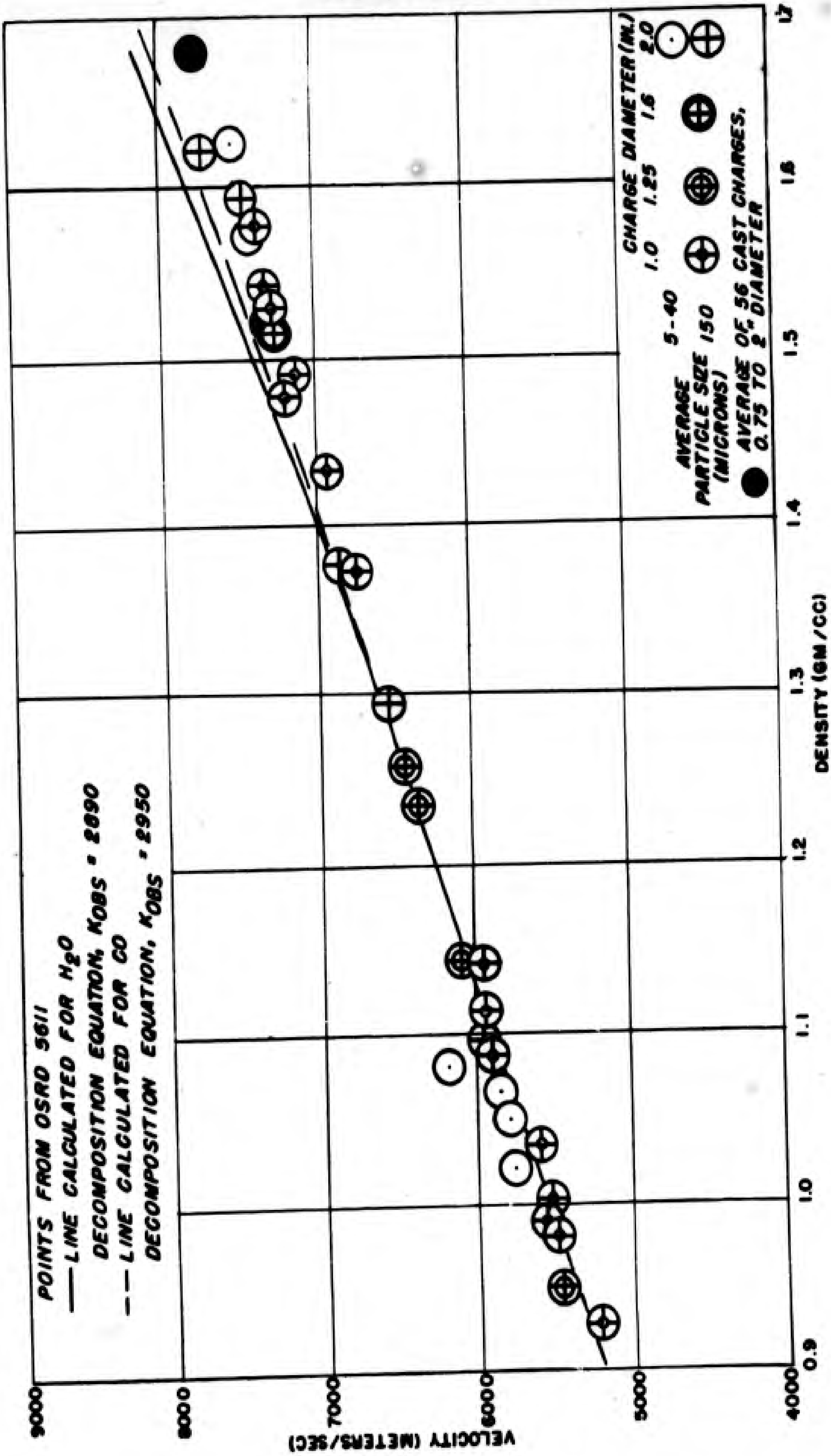


FIG. 3
COMPOSITION B

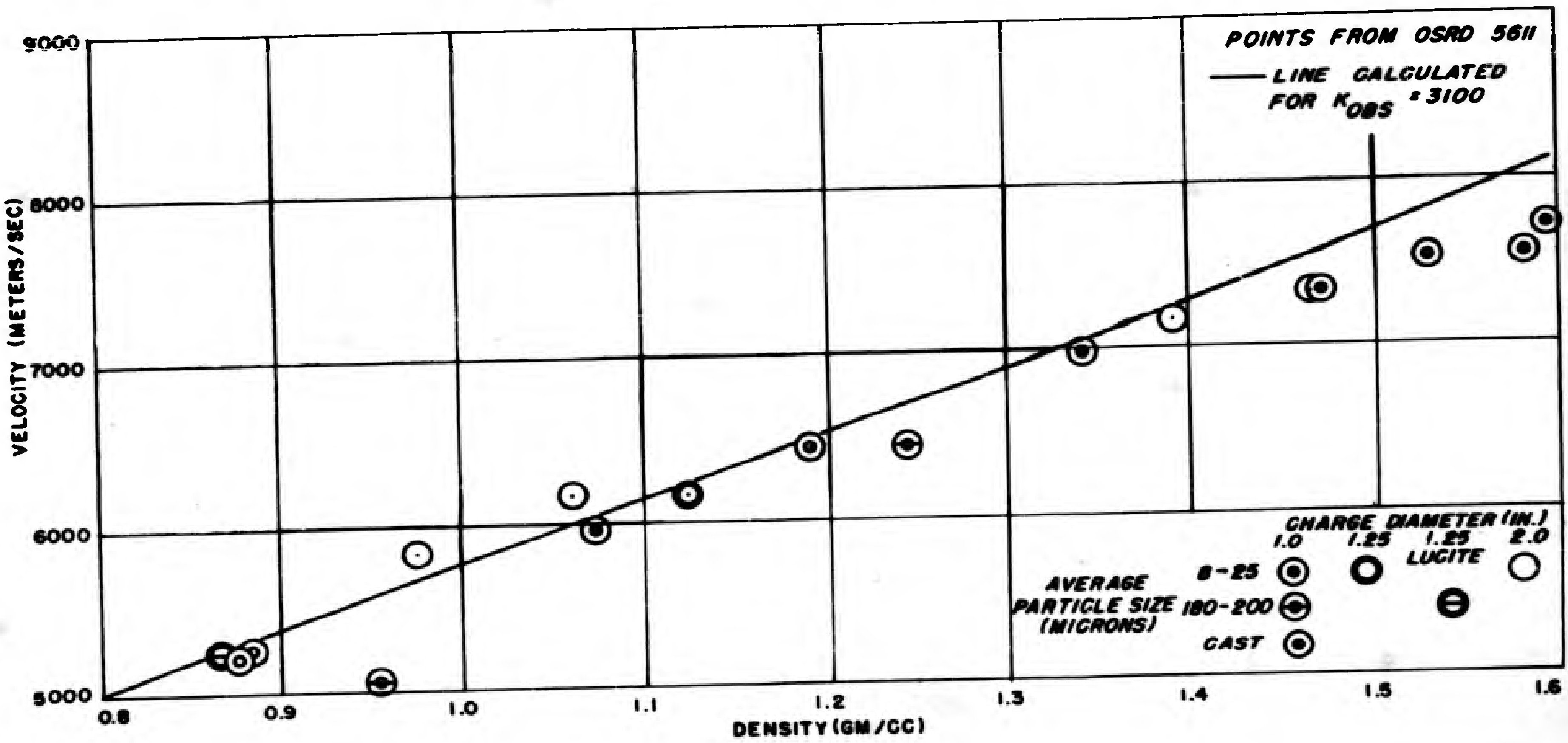

POINTS FROM OSRD 5611
LINE CALCULATED FOR K_{OBS} = 3100
CHARGE DIAMETER (IN.)
1.0
1.25
1.25 LUCITE
2.0
AVERAGE PARTICLE SIZE (MICRONS)
8-25
180-200
CAST
VELOCITY (METERS/SEC)
9000
8000
7000
6000
5000
DENSITY (GM/CC)
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6

FIG. 4
DINA

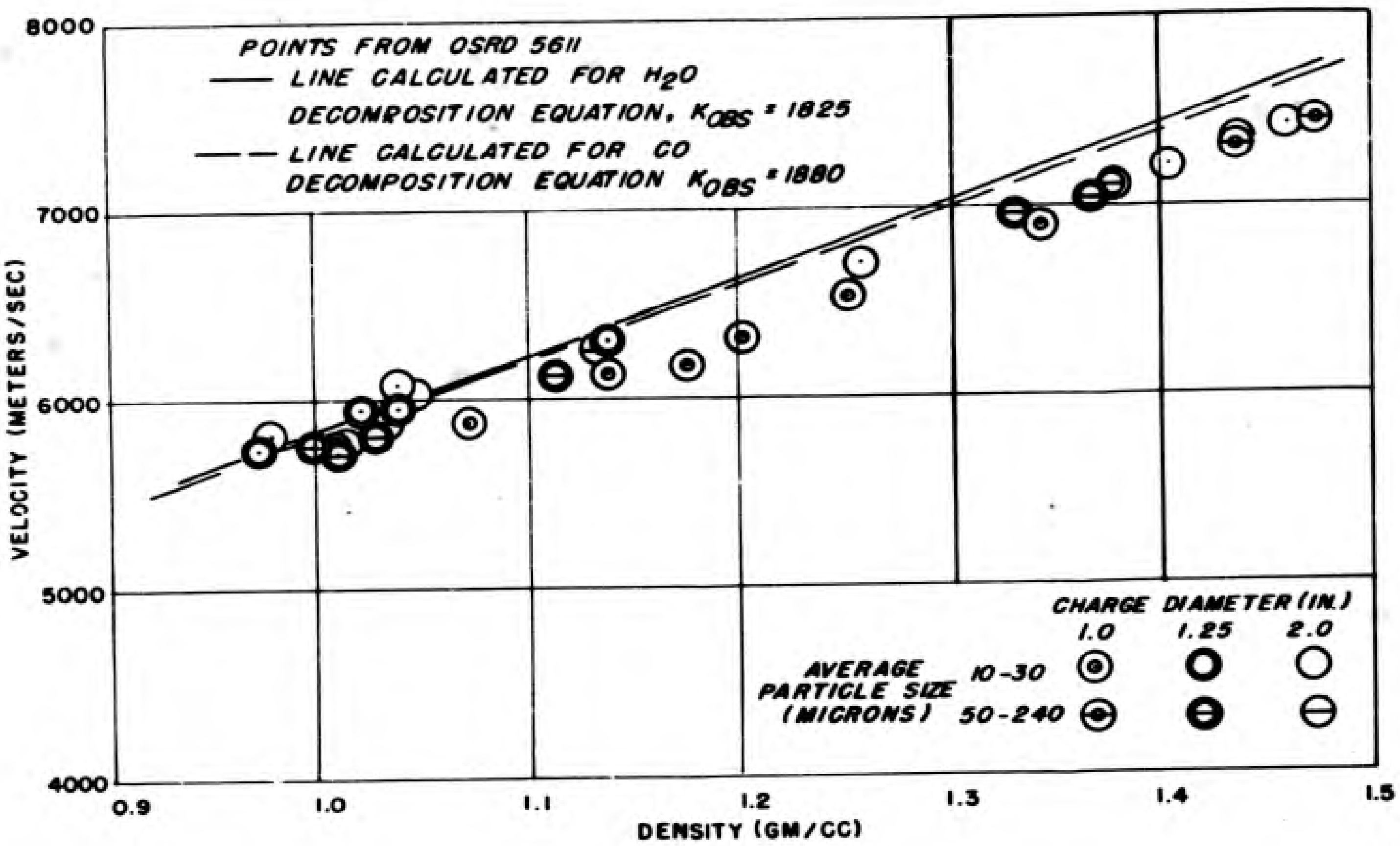


FIG. 5
EDNA (HALEITE)

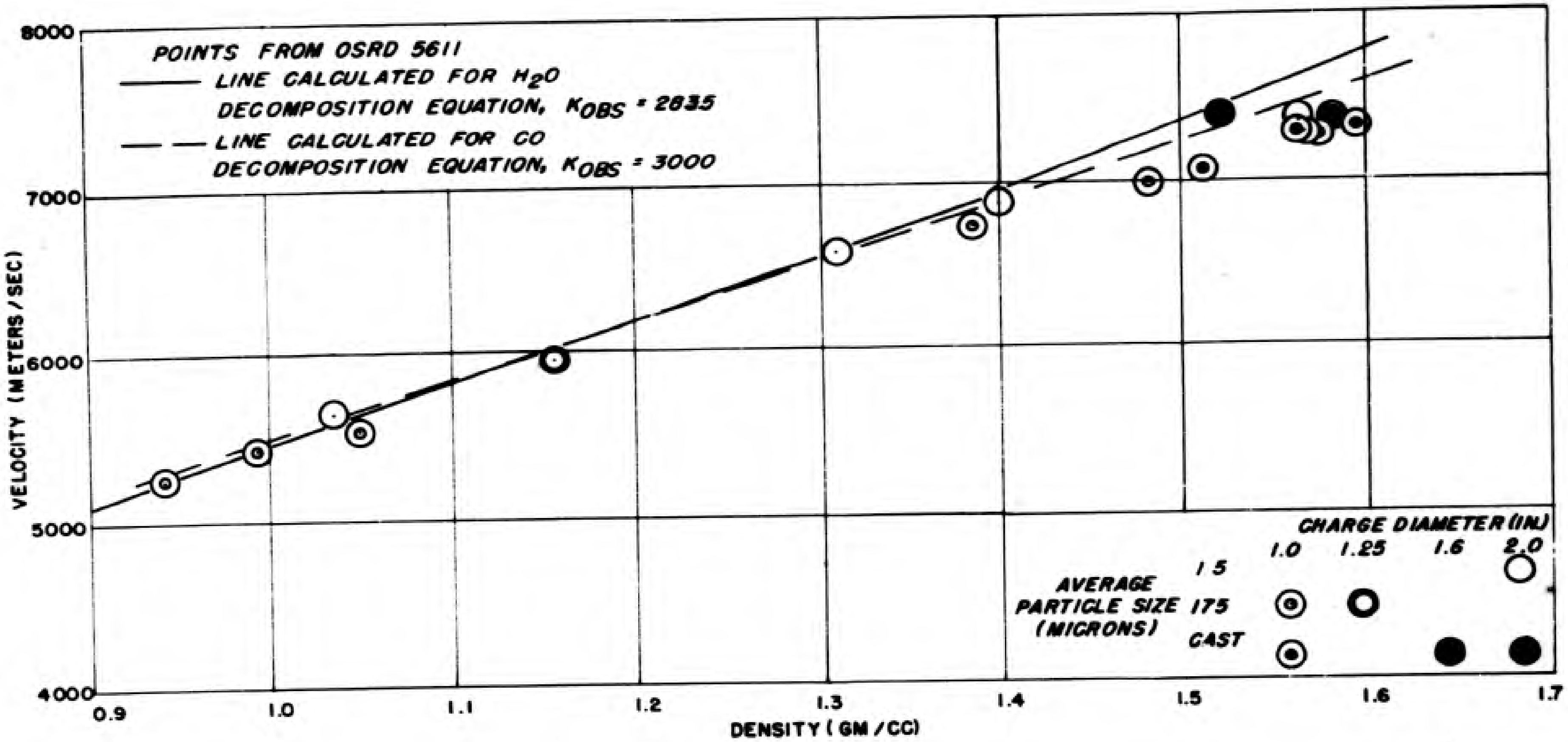


FIG. 6

EDNATOL (60/40 EDNA/TNT)

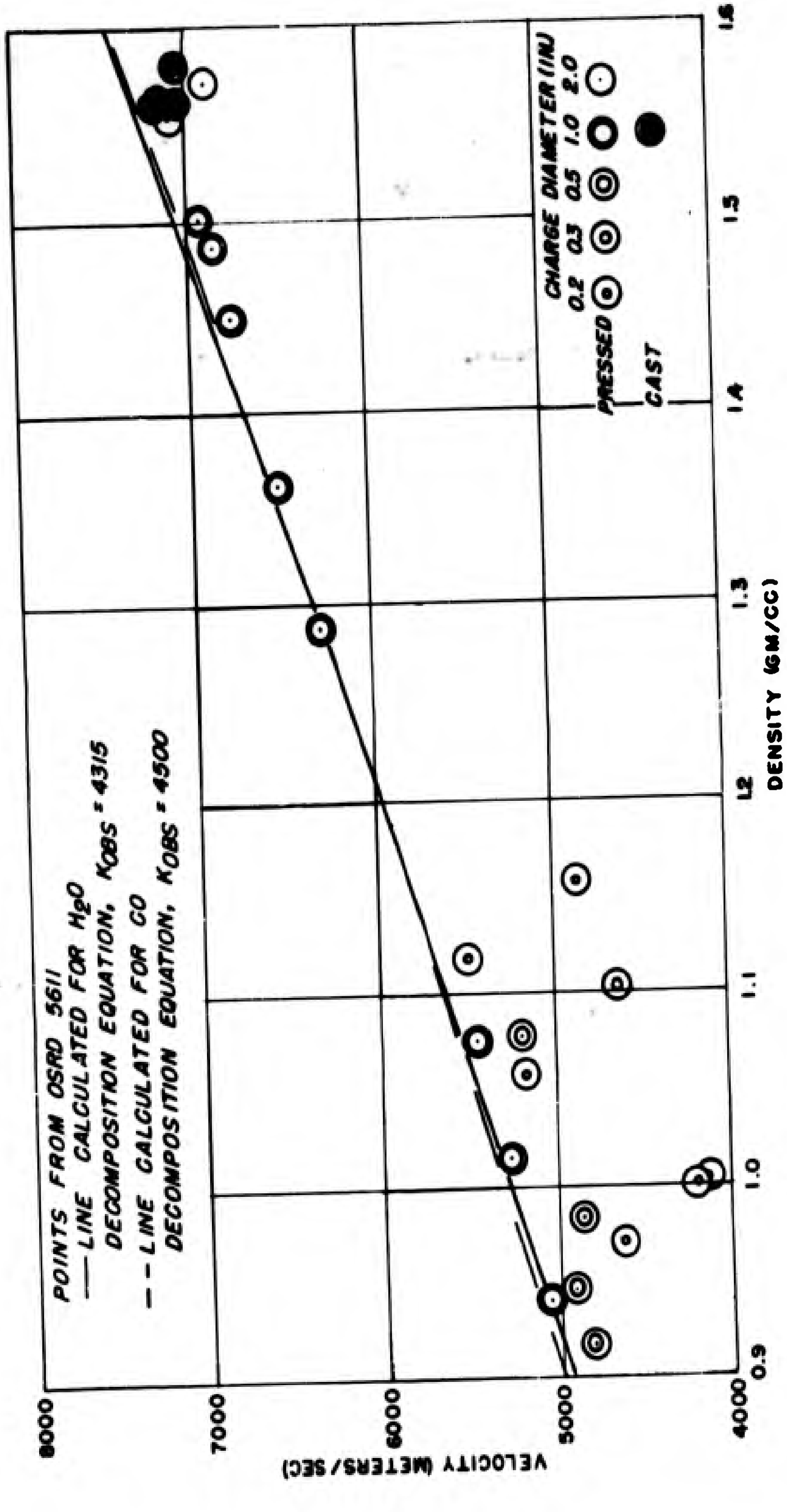


FIG. 7
FIVONITE

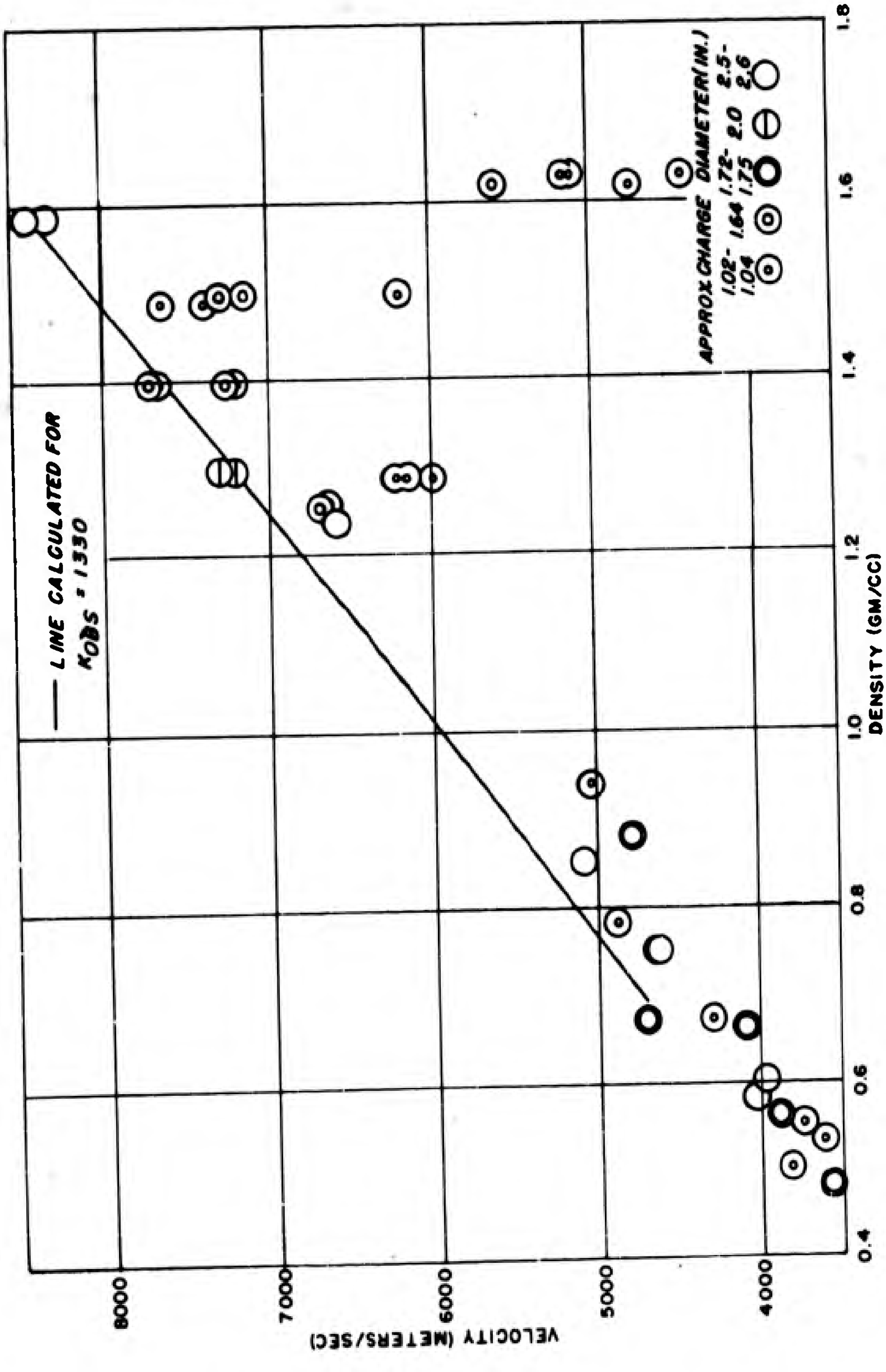


FIG. 8
HYDRAZINE NITRATE

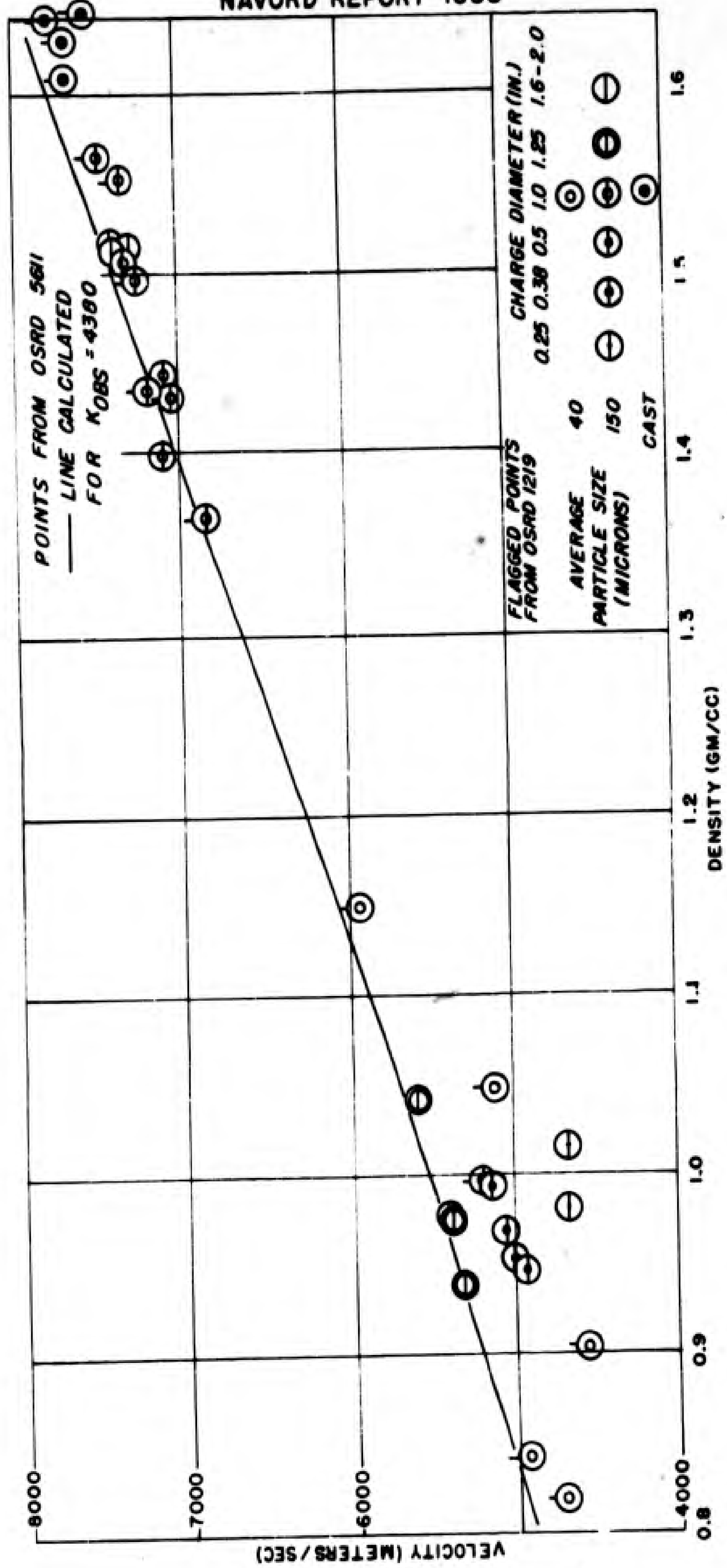

POINTS FROM OSRD 5611
— LINE CALCULATED
FOR K_{OBS} = 4380
FLAGGED POINTS FROM OSRD 1219
AVERAGE PARTICLE SIZE (MICRONS)
40
150
CAST
CHARGE DIAMETER (IN.)
0.25 0.38 0.5 1.0 1.25 1.6-2.0
VELOCITY (METERS/SEC)
8000
7000
6000
4000
DENSITY (GM/CC)
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6

FIG. 9
NENO

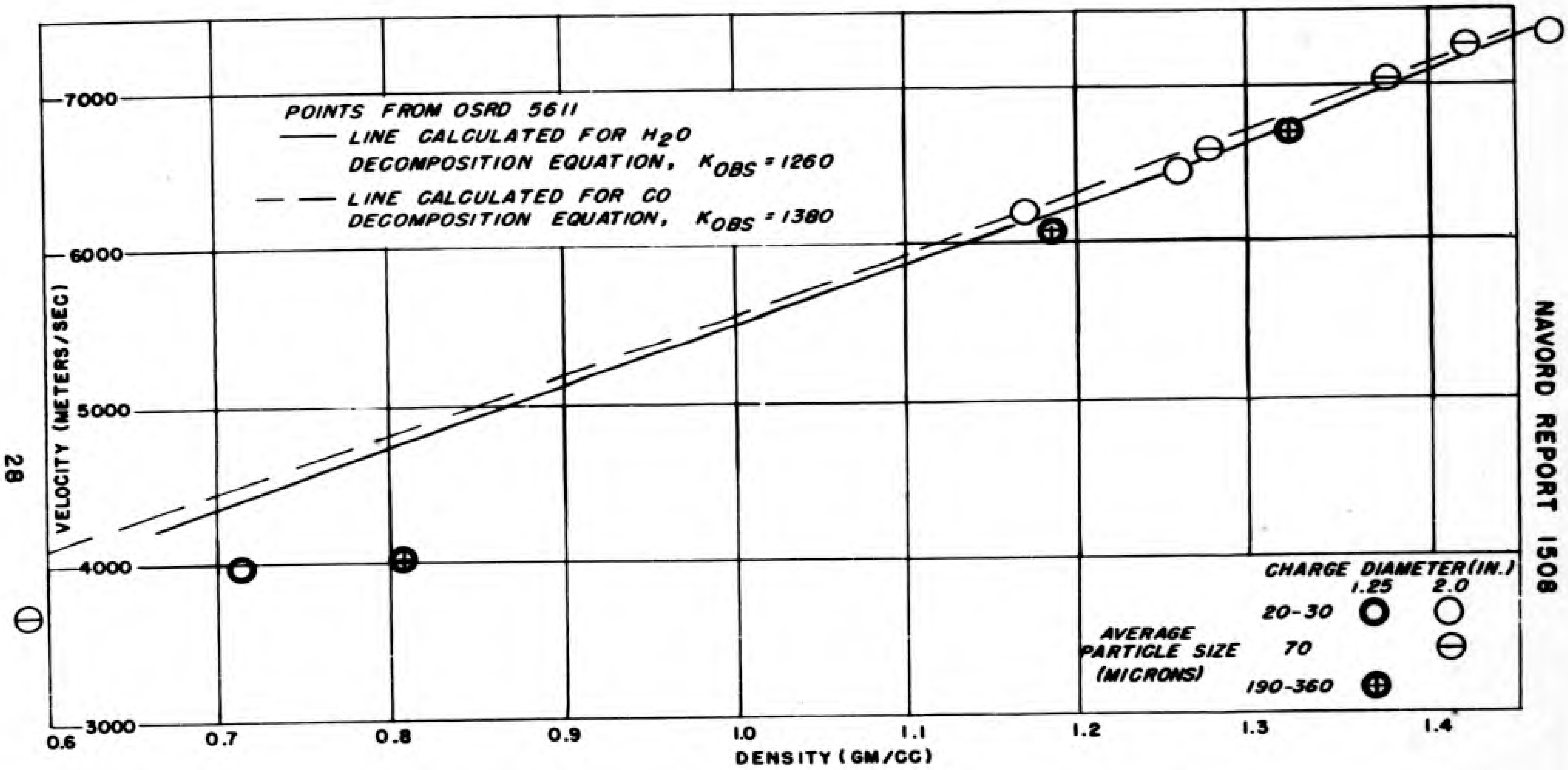


FIG. 10
NITROGUANIDINE

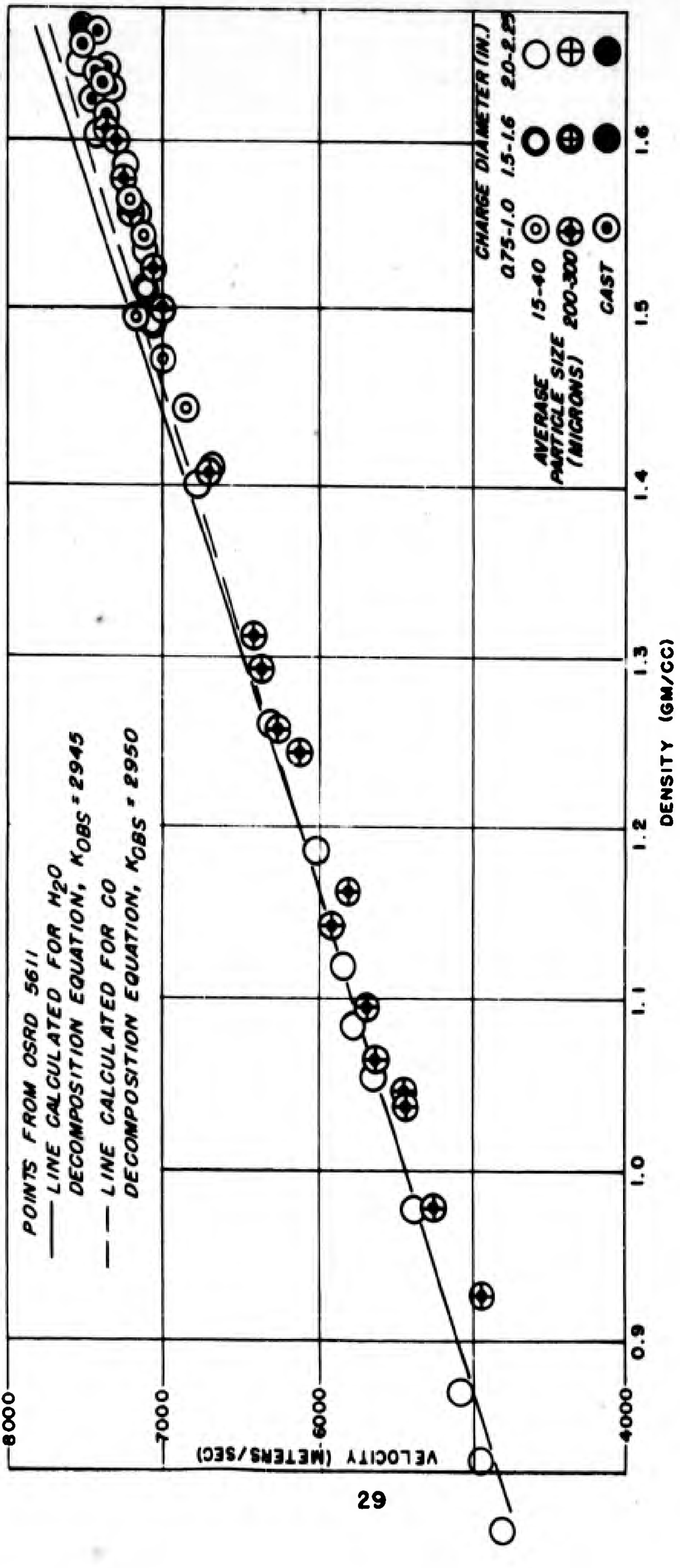


FIG. 11
PENTOLITE

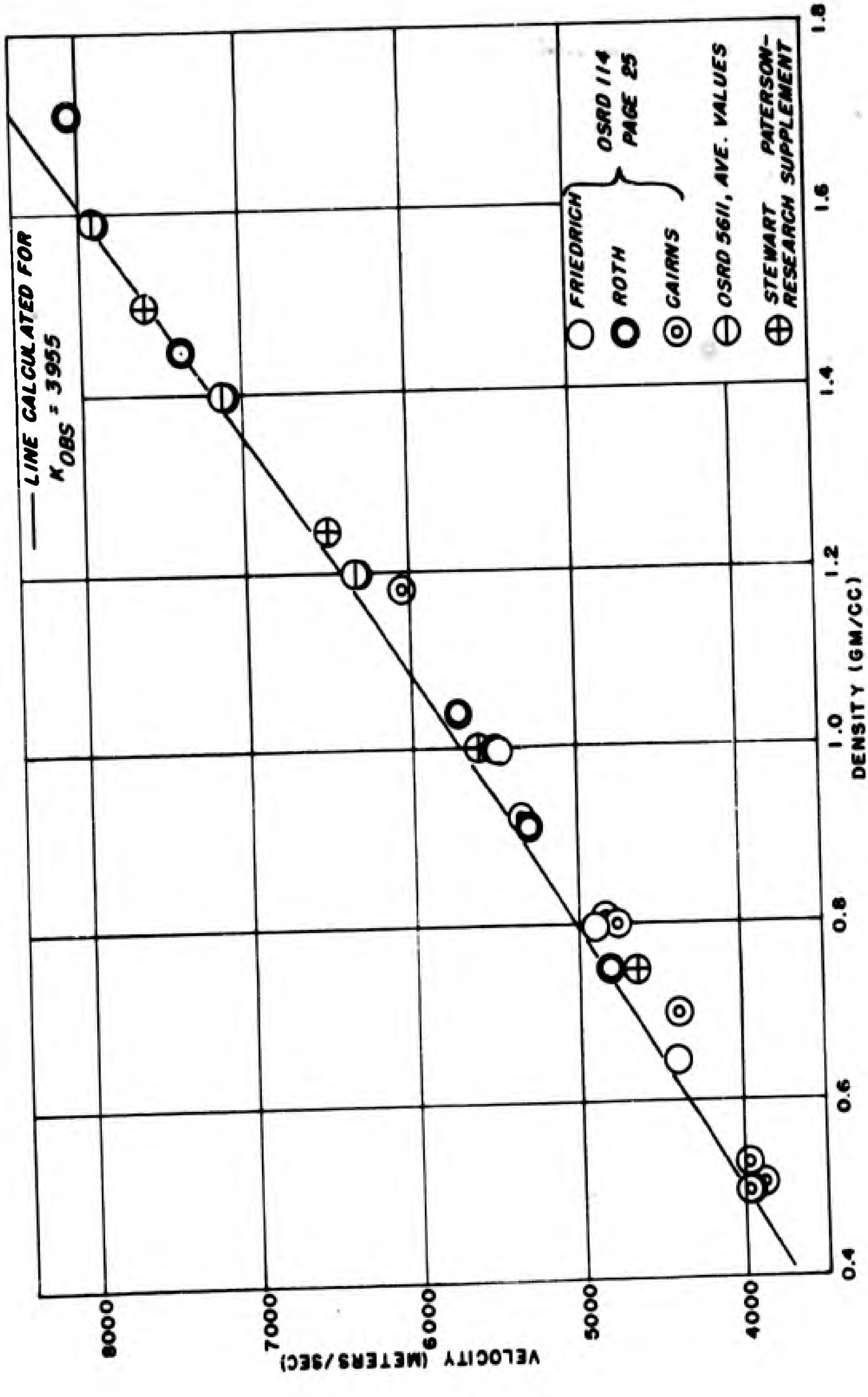

LINE CALCULATED FOR $K_{OBS} = 3955$
FRIEDRICH
ROTH
OSRD 114 PAGE 25
CAIRNS
OSRD 5611, AVE. VALUES
STEWART, PATERSON-RESEARCH SUPPLEMENT
VELOCITY (METERS/SEC)
8000
7000
6000
5000
4000
DENSITY (GM/CC)
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8

FIG. 12
PETN

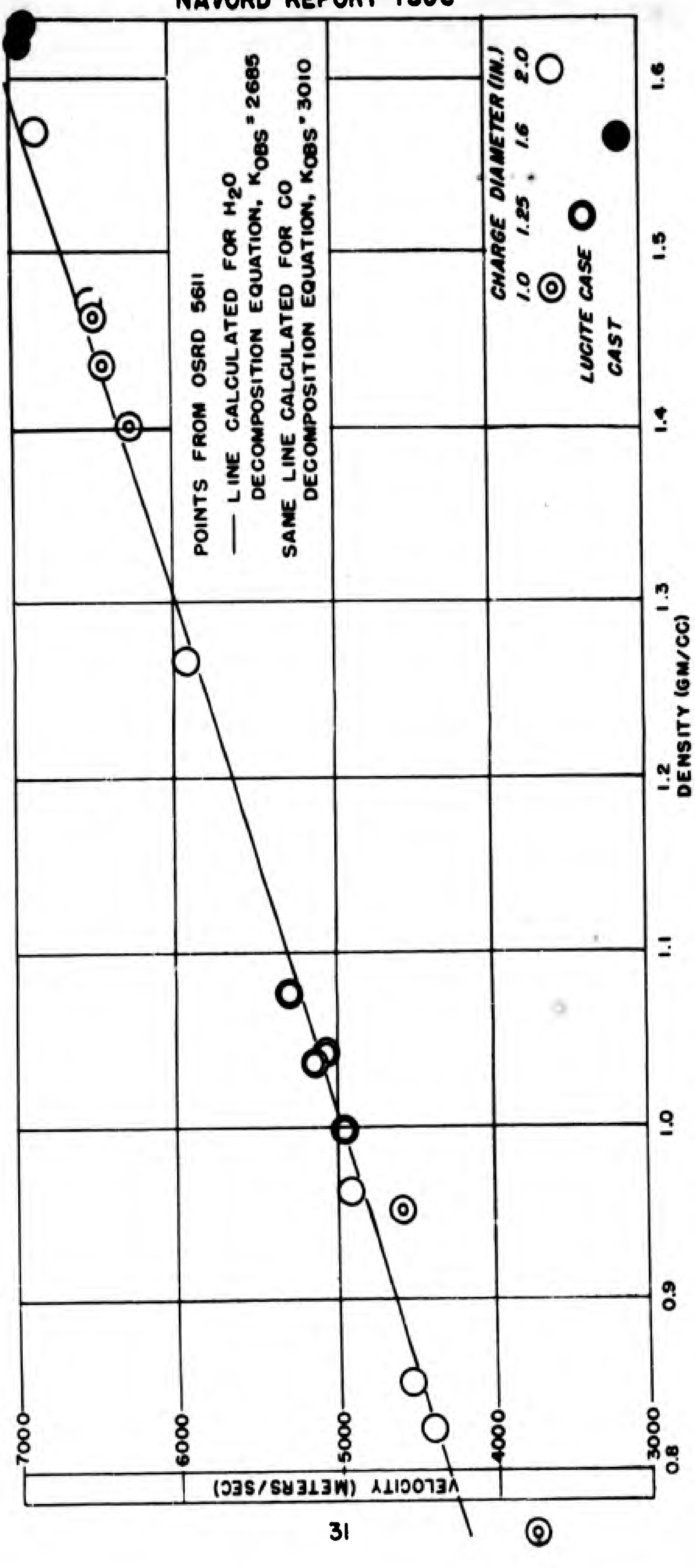


FIG. 13

PICRATOL (50/50, AMMONIUM PICRATE/TNT)

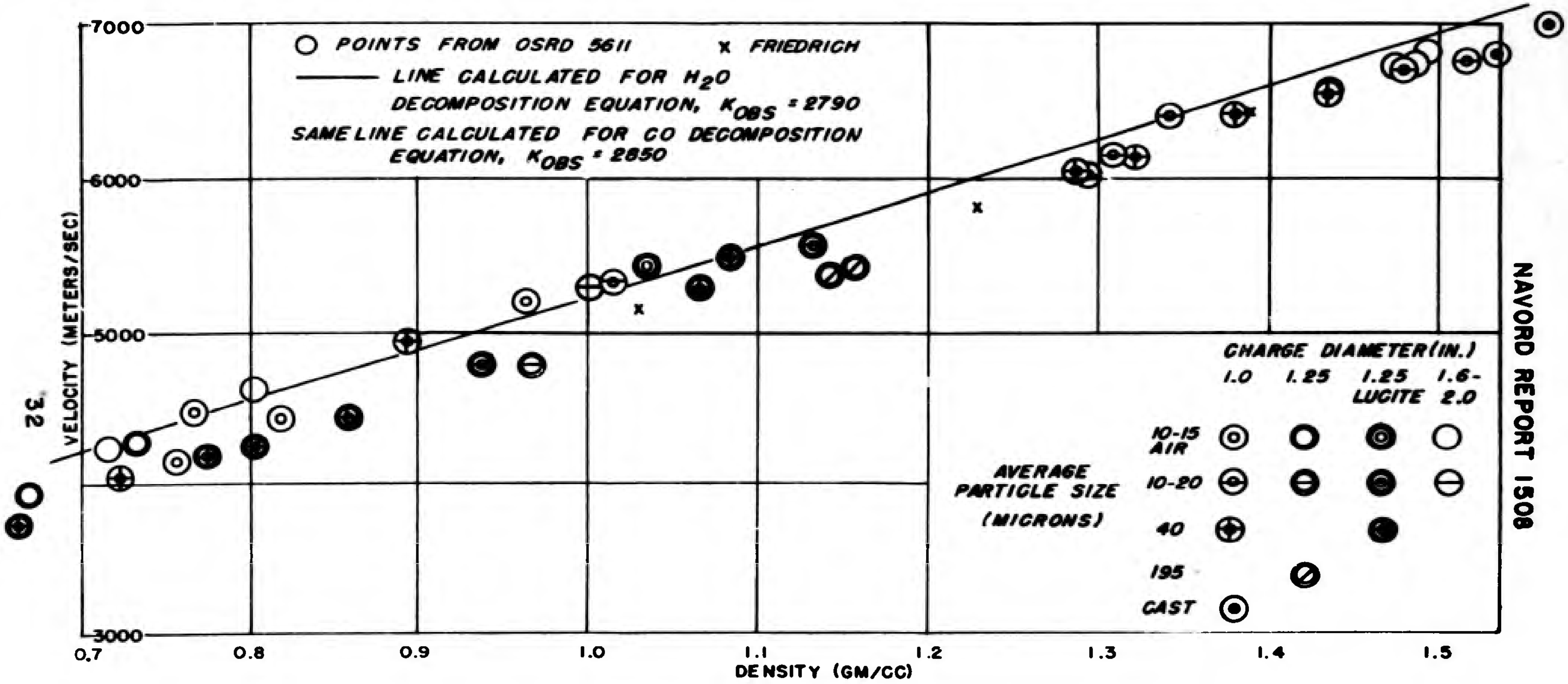


FIG. 14
PICRIC ACID

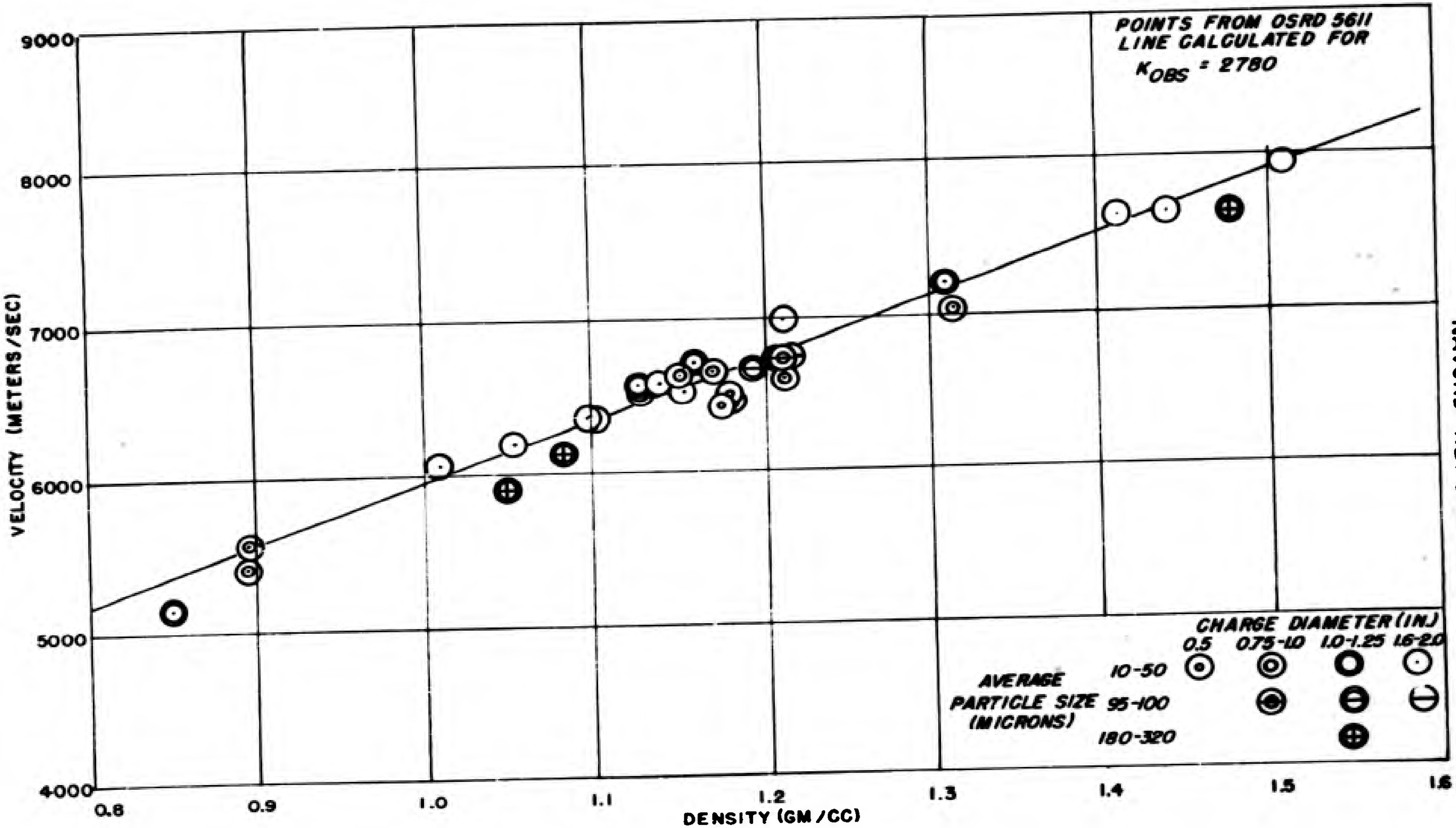

POINTS FROM OSRD 5611
LINE CALCULATED FOR
$K_{OBS} = 2780$
CHARGE DIAMETER (IN.)
0.5
0.75-1.0
1.0-1.25
1.6-2.0
AVERAGE
PARTICLE SIZE
(MICRONS)
10-50
95-100
180-320
VELOCITY (METERS/SEC)
9000
8000
7000
6000
5000
4000
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
DENSITY (GM/CC)

FIG. 15
RDX

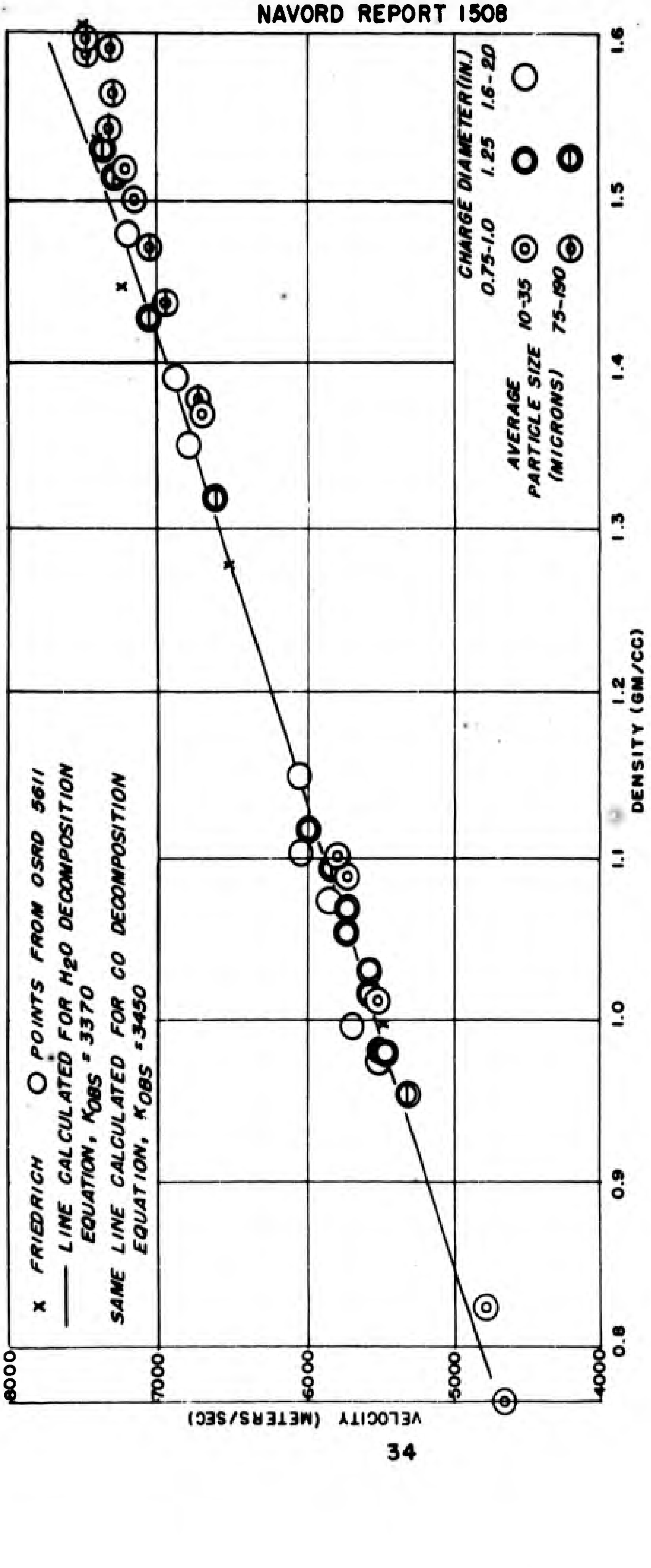


FIG. 16
TETRYL

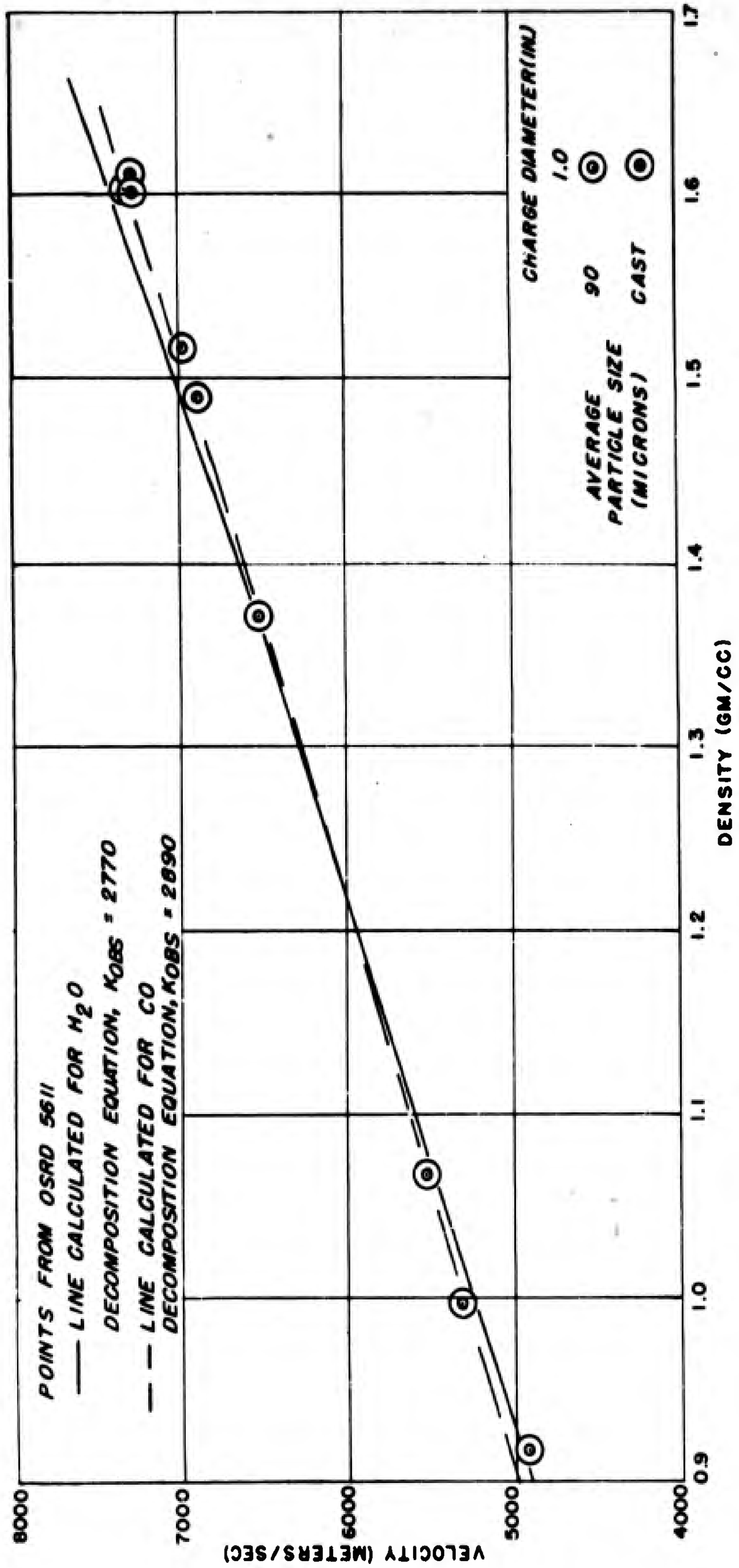


FIG. 17
TETRYTOL (70/30 TETRYL/TNT)

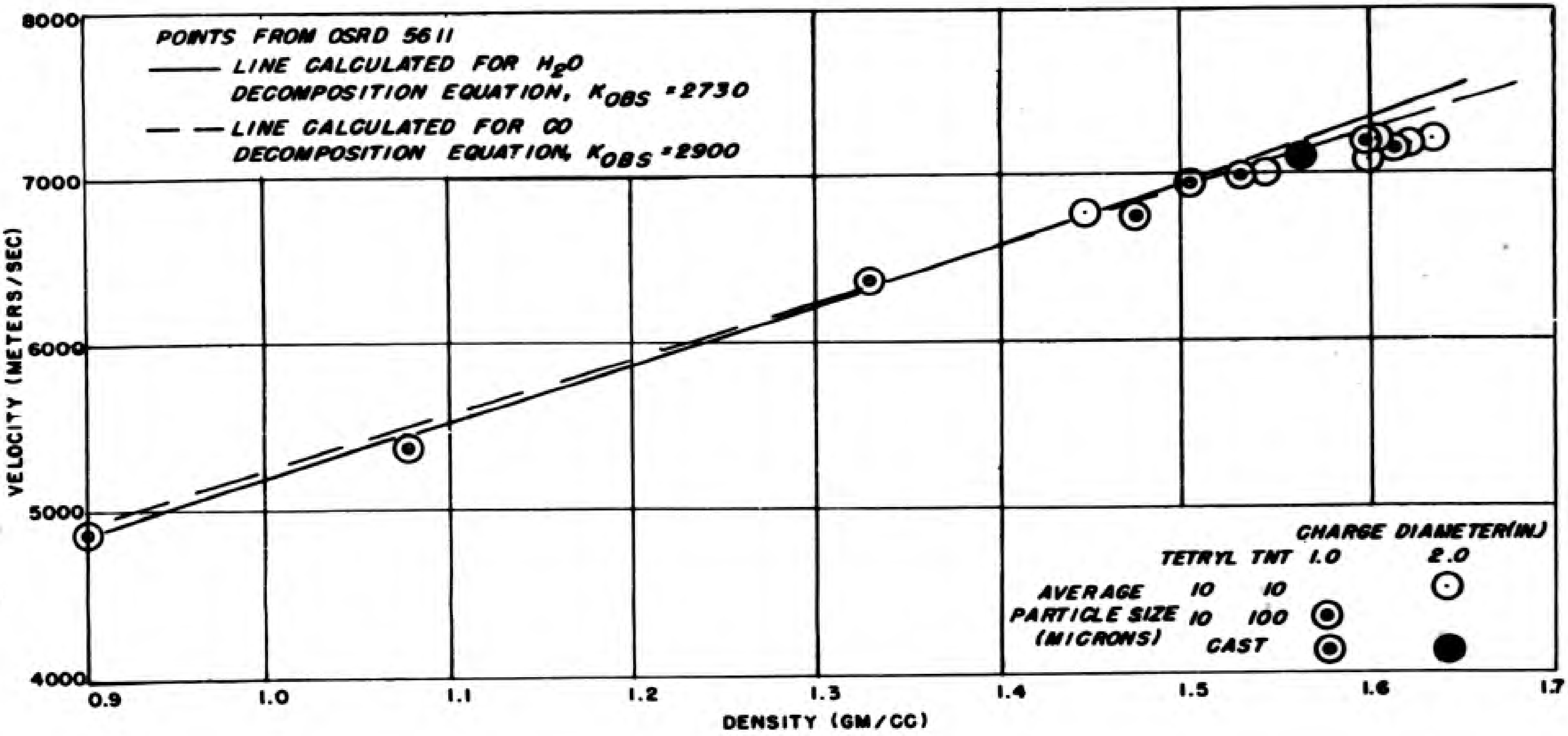


FIG. 18
TETRYTOL (60/40 TETRYL/TNT)

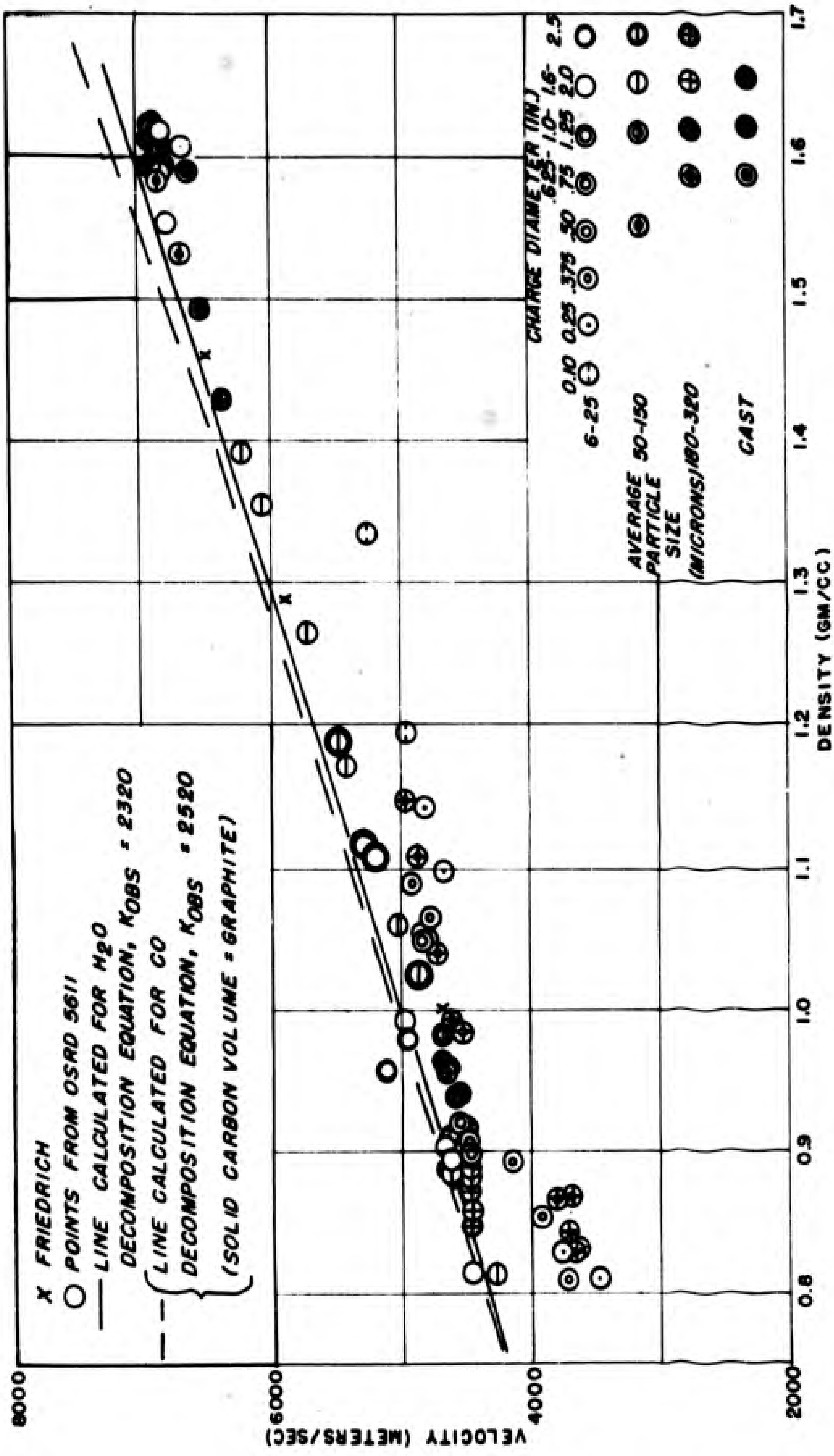
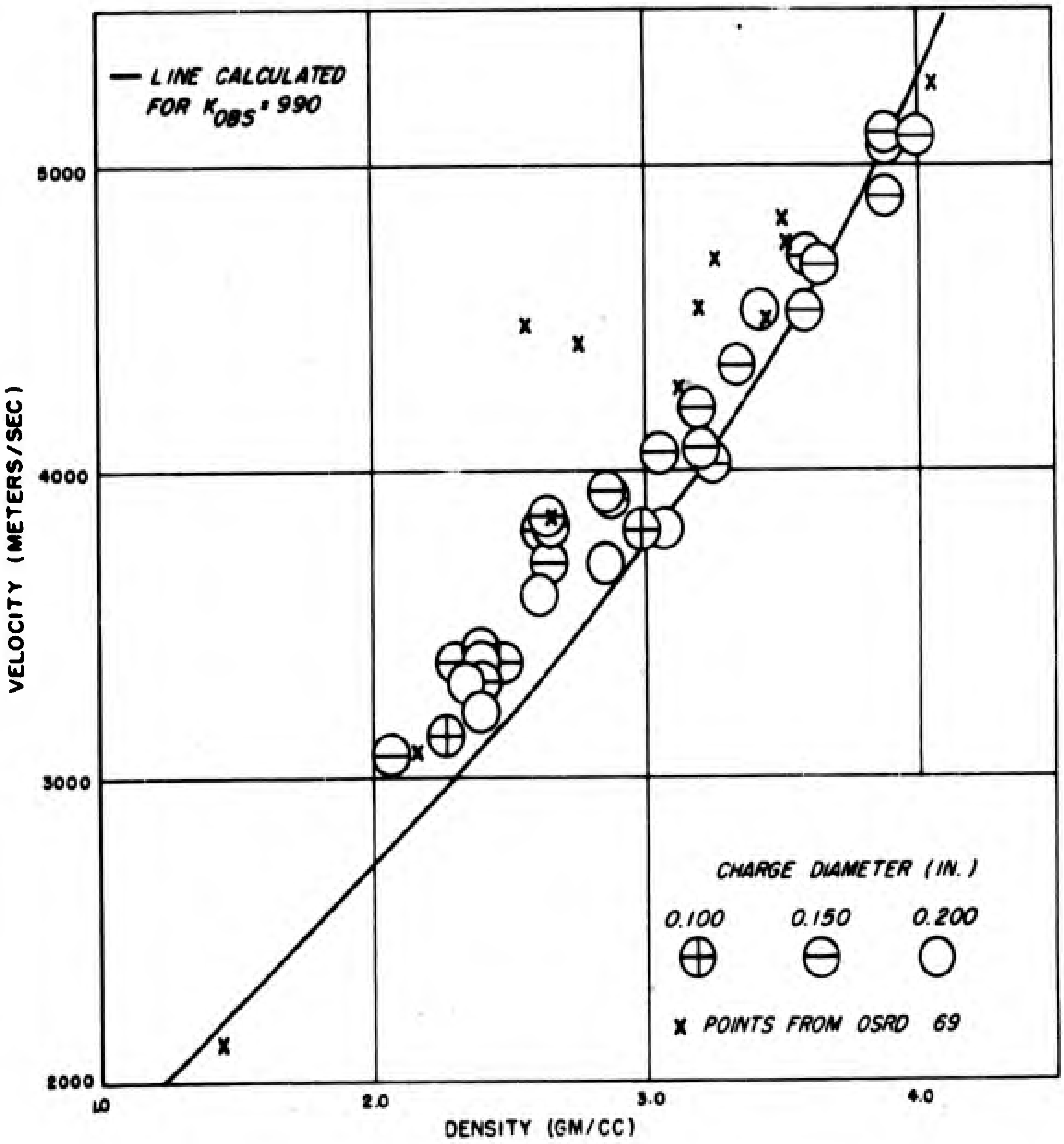

X FRIEDRICH
○ POINTS FROM OSRD 5611
— LINE CALCULATED FOR H_2O DECOMPOSITION EQUATION, K_{OBS} = 2320
– – LINE CALCULATED FOR CO DECOMPOSITION EQUATION, K_{OBS} = 2520 (SOLID CARBON VOLUME = GRAPHITE)
CHARGE DIAMETER (IN.)
0.10
0.25
.375
.50
.75
.625-1.0-1.25
1.6-2.0
2.5
AVERAGE PARTICLE SIZE (MICRONS)
6-25
50-150
180-320
CAST
VELOCITY (METERS/SEC)
8000
6000
4000
2000
DENSITY (GM/CC)
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7

FIG. 19
TNT

FIG. 20
LEAD AZIDE



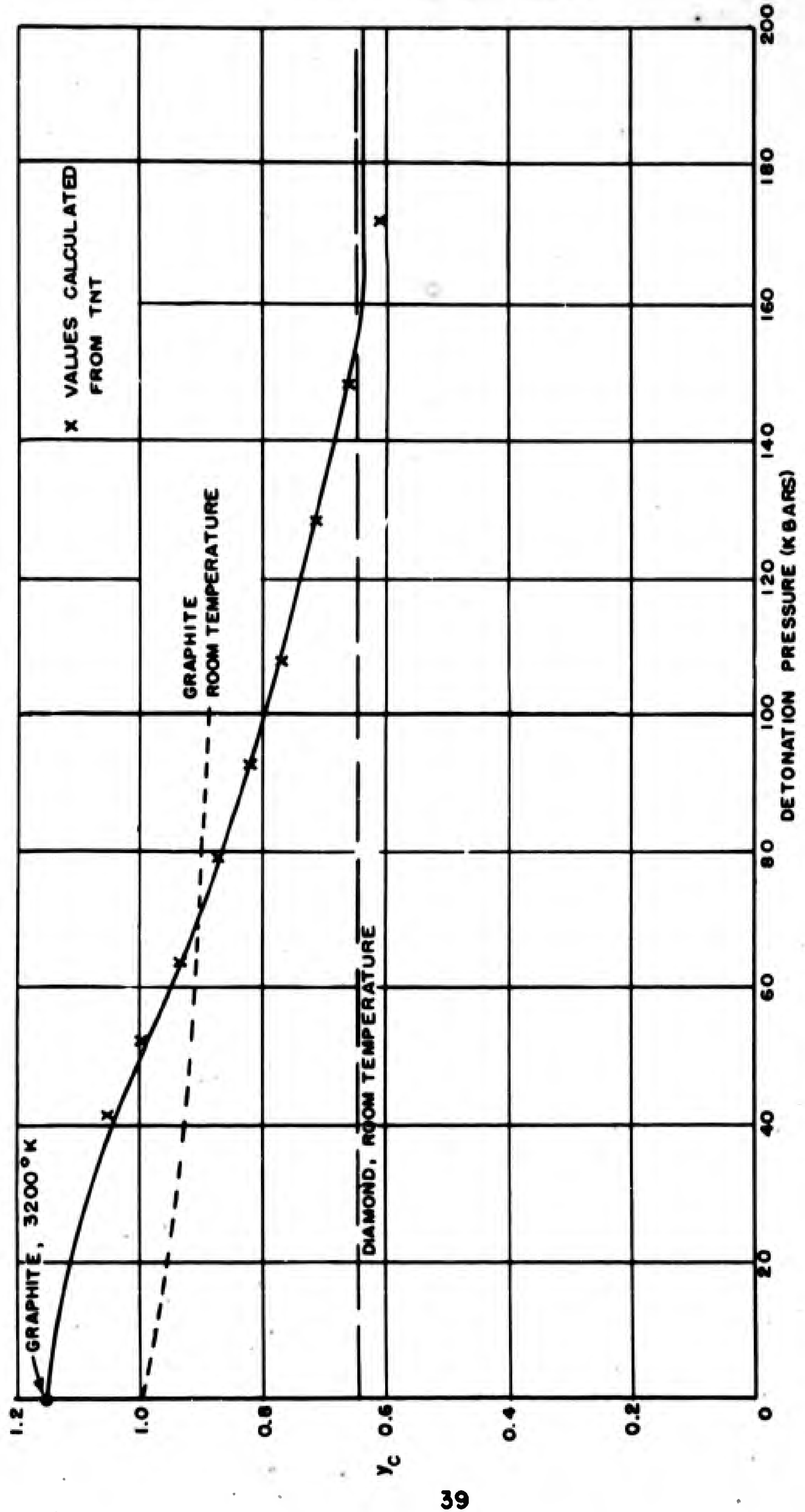


FIG. 21
VOLUME CORRECTION FOR SOLID CARBON

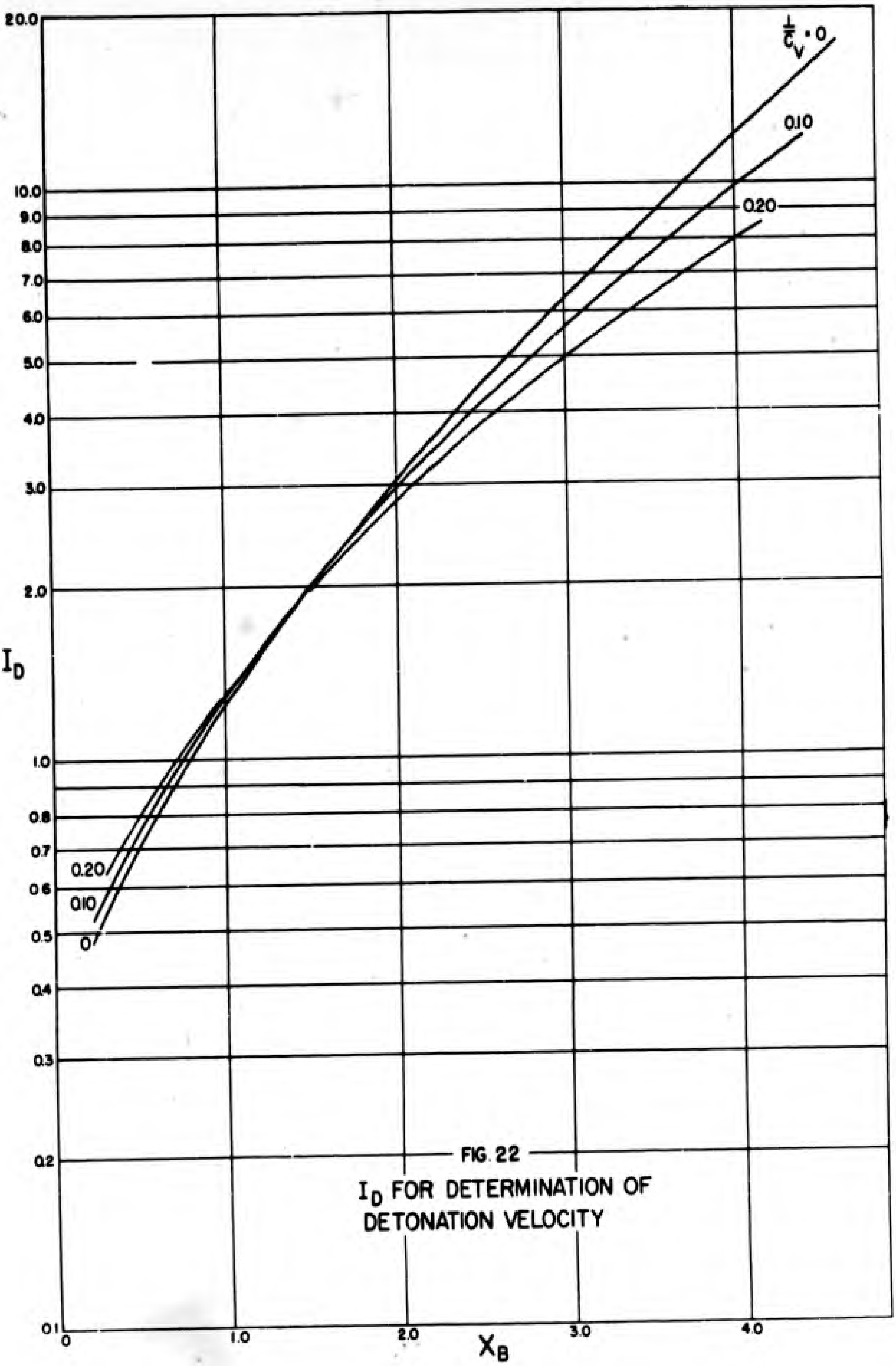


FIG. 22

I_D FOR DETERMINATION OF DETONATION VELOCITY

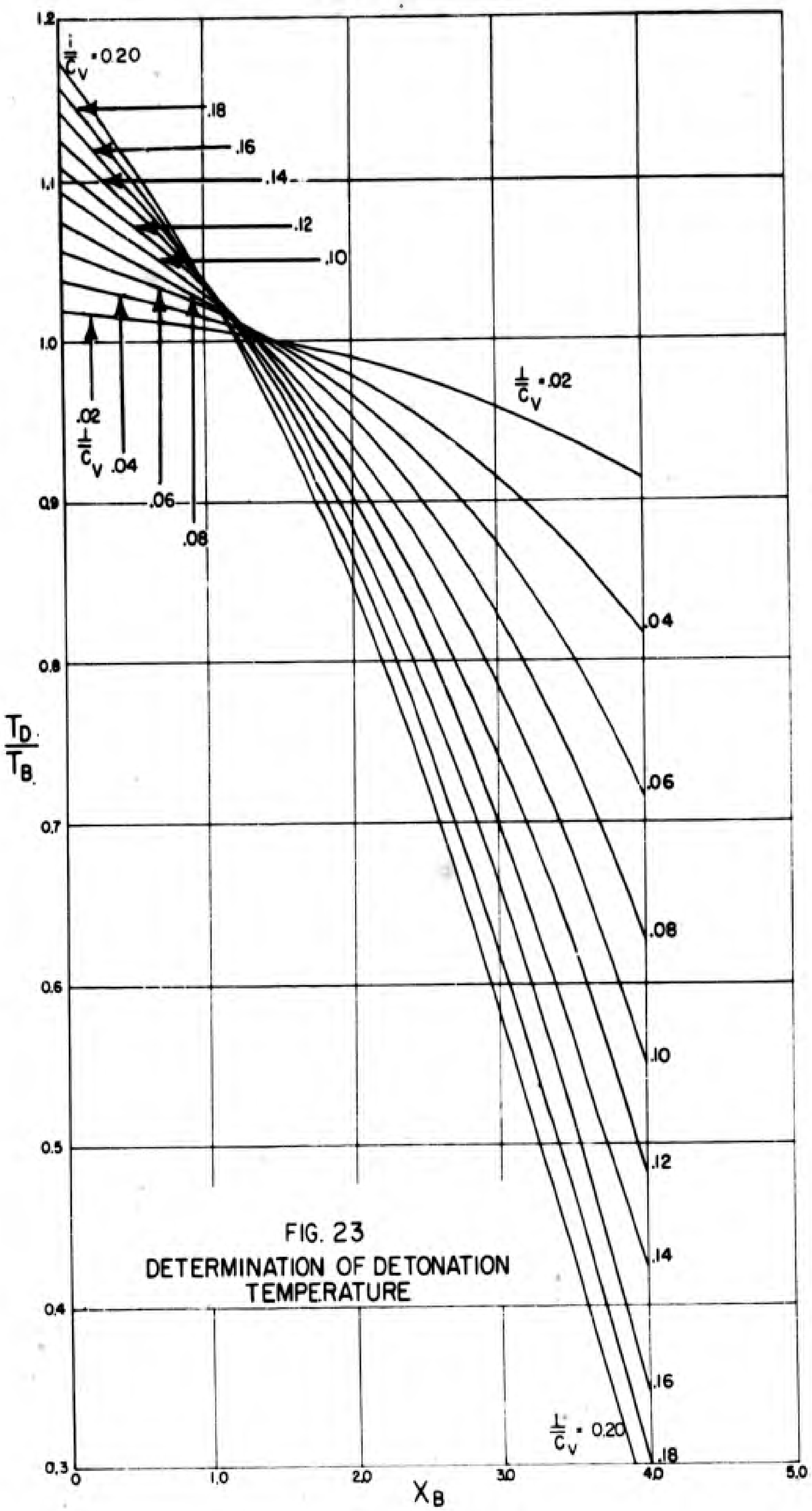


FIG. 23
DETERMINATION OF DETONATION TEMPERATURE

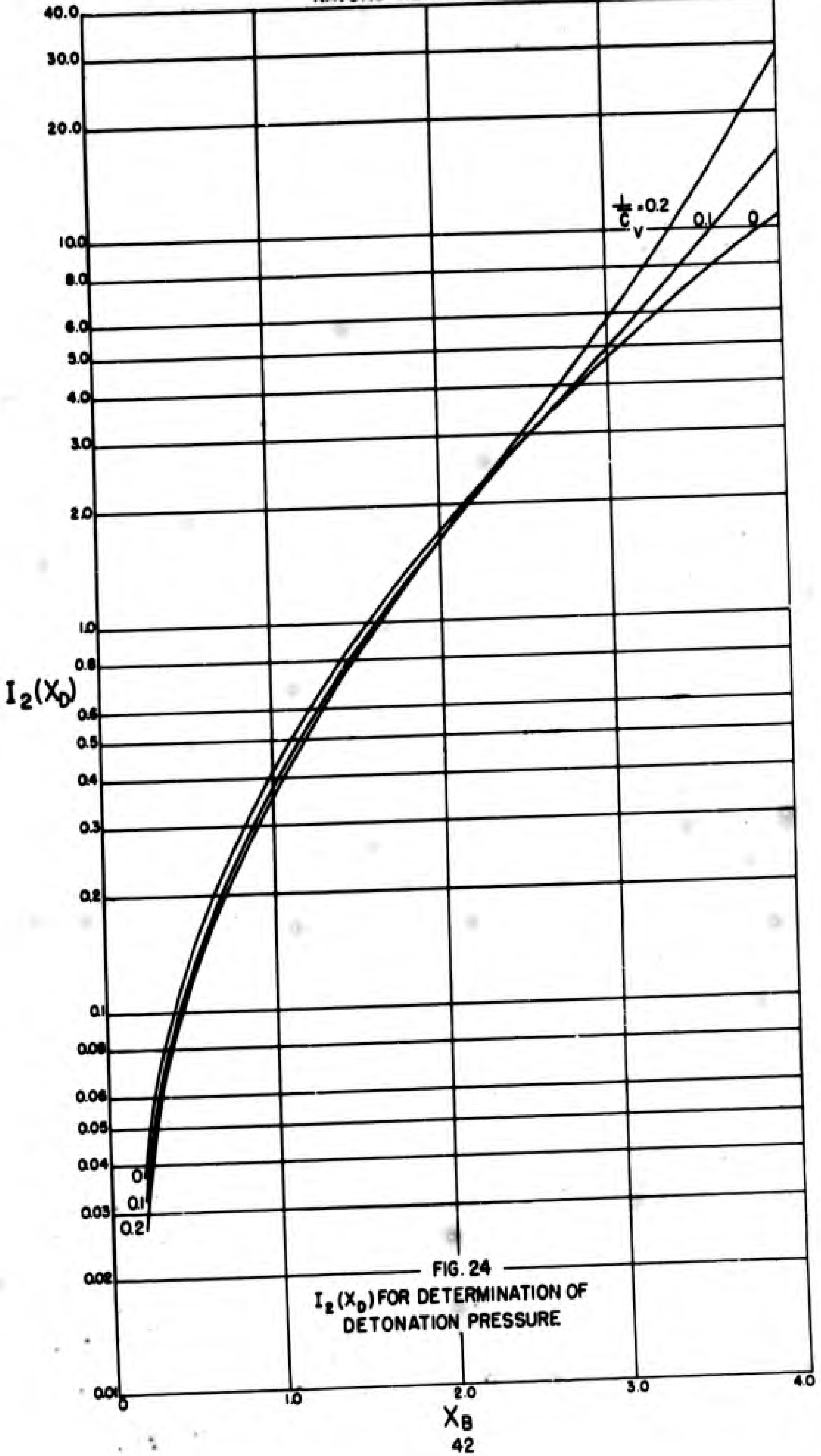


FIG. 24
$I_2(X_D)$ FOR DETERMINATION OF DETONATION PRESSURE

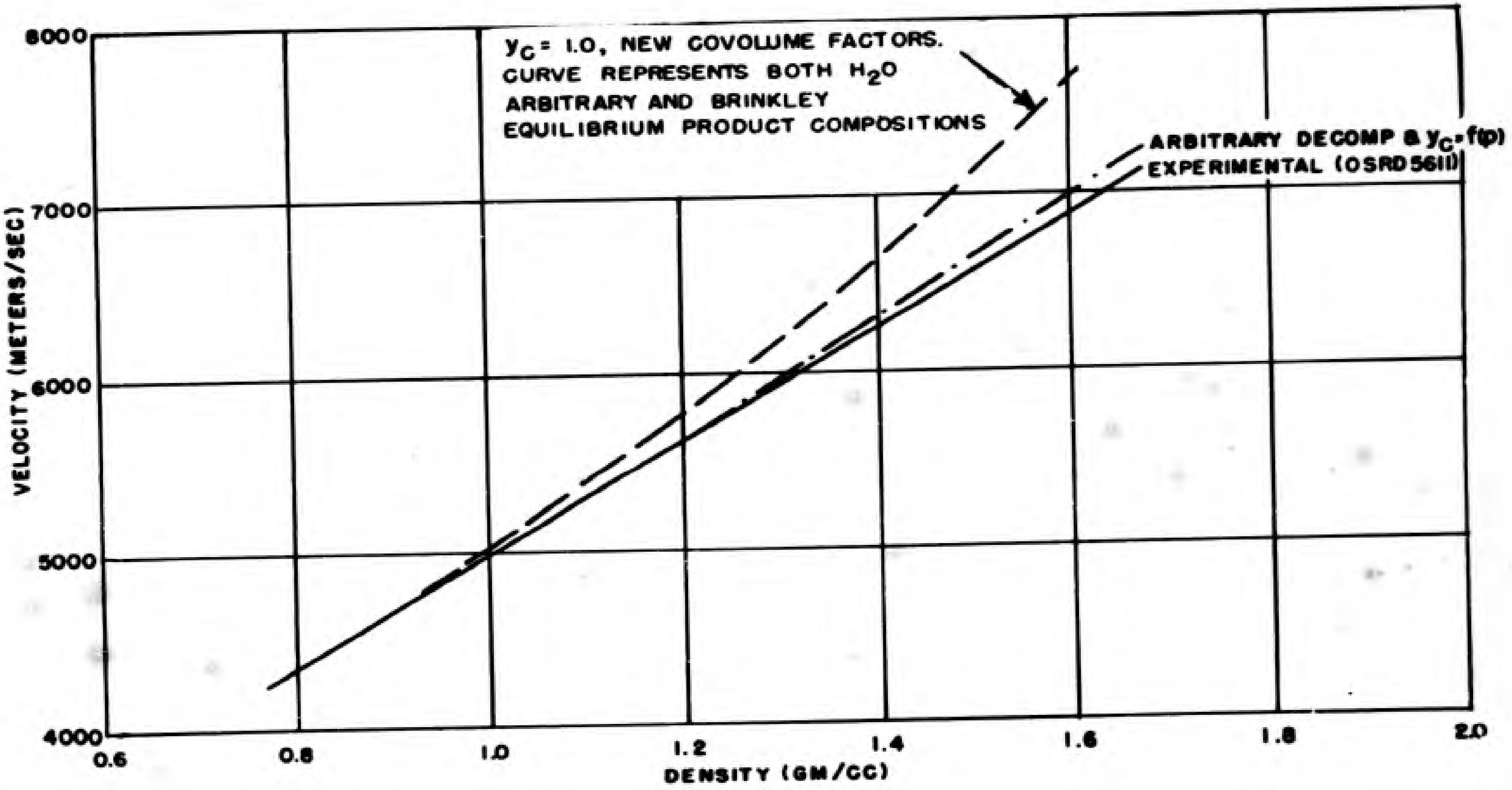
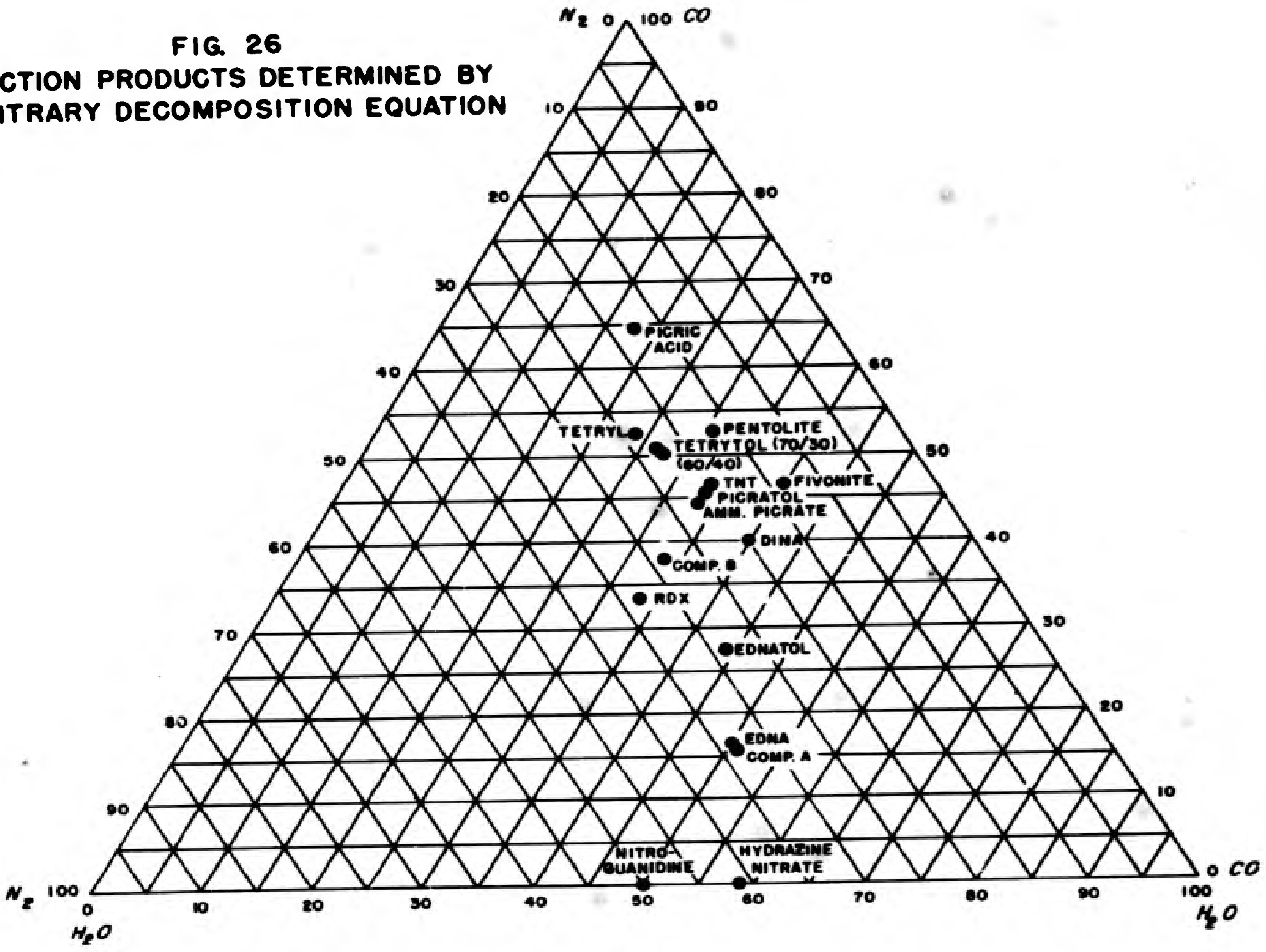


FIG. 25

EFFECT OF VOLUME CORRECTION FOR CARBON UPON DETONATION VELOCITIES OF TNT

FIG. 26
REACTION PRODUCTS DETERMINED BY
H_2O ARBITRARY DECOMPOSITION EQUATION



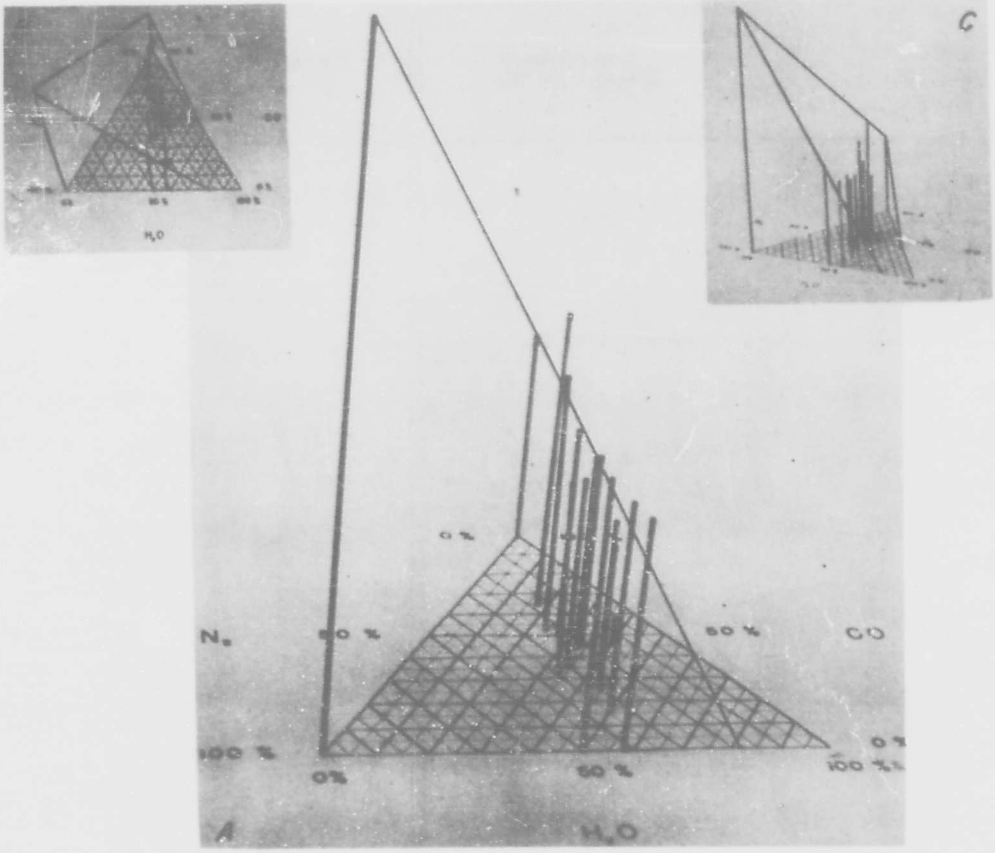


Figure 27. Three-dimensional model of covolume factors.
(Lead Azide omitted)

The triangular plot of decomposition products is the same as that of fig. 26. For each explosive located in the triangular plot, the length of shaft shown represents

$$\bar{k} = k_{obs.}/n_g$$

The plot itself is taken at the level of $\bar{k} = 275$, i.e., each shaft actually pictures ($\bar{k}$ - 275). Values of $\bar{k} = 287$ (Pivonite) and $\bar{k} = 328$ (Picric Acid) are represented by the shortest and longest shafts shown; all others lie between these two in length.

The shafts at the vertices of the triangular plot represent the species covolume factors calculated for H_2O, N_2 and CO by least squares, with lead azide omitted (see paragraph 4). These values are: $k_{N_2} = 389$, $k_{CO} = 314$ and $k_{H_2O} = 249$. Since k_{H_2O} is less than 275, the level of the plot, it is negative with respect to the reference level. A thread connects the tips of the shafts representing N_2, H_2O and CO. The distances of the various shaft tips above and below the plane indicated by this thread are proportional to the differences (scatter) between $k_{obs.}$ and $\sum n_i k_i$ for this particular set of k_i. The relationships here presented pictorially are shown in Table III, col. 1 ($k_{obs.}$), col. 2 ($\sum n_i k_i$) and col. 3 (δ).

In view A, the model is so oriented that the plane delineated by the connecting thread is shown as a line. In the inset views B and C, the model is shown from two angles above the plane. Note the narrow range of explosives which provide experimental "support" for the plane. It is apparent that this plane could be tipped radically along the CO - H_2O median (i.e., the value of the N_2 vertex lowered, and that of the H_2O vertex raised) without appreciable change of its level in the region of experimental points.

TABLE IA. Explosive Parameters-H_2O Arbitrary Decomposition Equation

	Composition (gm-atoms per $M_o$gm)				Decomposition Products (gm-mol. per M_o gms)					
Explosive	C	H	N	O	H_2O	CO	CO_2	N_2	O_2	C
1. Ammonium Picrate	6	6	4	7	3	4	—	2	--	2
2. Composition A	4.672	9.346	6.140	6.140	4.673	1.467	--	3.070	--	3.205
3. Composition B	5.104	6.250	5.37	6.69	3.125	3.565	—	2.685	—	1.539
4. DINA*	4	8	4	8	4	4	—	2	--	—
5. EDNA (Haleite)	2	6	4	4	3	1	—	2	—	1
6. Ednatol (60/40)	5.078	8.190	5.315	6.635	4.095	2.540	—	2.658	—	2.538
7. Pivonite	9	12	4	13	6	7	—	2	—	2
8. Hydrazine Nitrate*	—	5	3	3	2.5	—	—	1.50	0.25	--
9. NENO*	6	8	6	12	4	4	2	3	—	—
10. Nitroglycerine*	3	5	3	9	2.5	—	3	1.50	0.25	—
11. Nitroguanidine	1	4	4	2	2	—	--	2	--	1
12. Pentolite	5.825	5.91	3.23	8.04	2.955	5.085	—	1.615	—	0.74
13. PETN*	5	8	4	12	4	2	3	2	—	—
14. Picratol (50/50)	6.895	5.795	3.68	6.853	2.898	3.955	—	1.84	—	2.94
15. Picric Acid	6	3	3	7	1.5	5.5	—	1.5	—	0.5
16. RDX*	3	6	6	6	3	3	—	3	—	—
17. Tetryl	7	5	5	8	2.5	5.5	—	2.5	—	1.5
18. Tetrytol (70/30)	6.573	4.696	4.036	6.853	2.348	4.505	—	2.018	—	2.068
19. Tetrytol (60/40)	6.734	4.811	3.931	6.819	2.406	4.413	—	1.966	—	2.321
20. TNT	7	5	3	6	2.5	3.5	—	1.5	—	3.5
21. Lead Azide*	$[Pb(N_3)_2]$				$[Pb + 3N_2]$					
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)

* Entry numbers 4, 8, 9, 10, 13, 16, 21 have same decomposition products for both arbitrary decomposition equations.

Mo	n_g	η	Q (Mo·cal)	Q (cal/gm.)	HFE	$A\cdot10^3$	$B\cdot10^6$	$\Psi_{graph.}$	$k_{obs.}$	$\bar{k}$	h	
246.16	9	0.098	191.08	0.776	95.04	65.07	4.47	0.0434	2790	310	12.6	1
250	9.210	0.155	323.86	1.295	- 8.97	73.79	5.392	0.0684	2875	312	13.6	2
250	9.375	0.074	290.52	1.162	- 8.64	65.25	4.571	0.0329	2890	308	12.5	3
240.16	10	0	244.42	1.018	100	63.16	4.74	0	3100	310	12.9	4
150.12	6	0.080	179.58	1.196	24.2	43.09	3.28	0.0356	1825	306	13.3	5
250	9.293	0.122	280.64	1.122	29.90	70.56	5.072	0.0542	2835	305	12.9	6
384.25	15	0.063	390.62	1.016	153	103.92	7.47	0.0278	4315	287	12.0	7
95.08	4.25	0	87.03	0.915	60	27.80	2.30	0	1330	313	14.0	8
356.20	13	0	433.41	1.217	101.8	89.44	5.95	0	4380	337	12.3	9
227.11	7.25	0	349.47	1.539	82.7	58.70	3.56	0	2915	402	12.8	10
104.09	4	0.115	99.98	0.960	18	30.14	2.28	0.0513	1260	315	13.7	11
250	9.655	0.036	257.3	1.029	55.75	63.21	4.405	0.0158	2945	305	12.2	12
316.17	11	0	451.79	1.429	123	82.42	5.34	0	3955	360	12.5	13
250	8.693	0.142	223.41	0.894	55.37	67.42	4.516	0.0628	2685	309	12.5	14
229.2	8.5	0.026	185.86	0.811	53.5	53.48	3.475	0.0116	2790	328	12.5	15
222.15	9	0	280.58	1.263	-21.3	55.89	4.11	0	2780	309	12.5	16
287.25	10.5	0.062	307.66	1.071	- 9.3	70.80	4.715	0.0279	3370	321	12.5	17
250	8.871	0.099	263.4	1.054	- 1.4	63.77	4.220	0.0442	2770	312	12.3	18
250	8.785	0.112	263.7	1.055	- 0.9	64.52	4.260	0.0496	2730	311	12.3	19
227.16	7.5	0.185	229.91	1.012	13	62.54	4.085	0.0822	2320	309	12.5	20
291.27	3	0.712	113.00	0.388	-111.	23.10	1.11	0	990	330	11.8	21
(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	

TABLE IB - Explosive Parameters - CO Arbitrary Decomposition Equation

	Composition				Decomposition Products						
Explosive	C	H	N	O	H_2O	CO	CO_2	N_2	H_2	O_2	C
1. Ammonium Picrate	6	6	4	7	1	6	-	2	2	-	-
2. Composition A.	4.672	9.346	6.140	6.140	1.468	4.672	-	3.070	3.205	-	-
3. Composition B.	5.104	6.250	5.37	6.69	1.586	5.104	-	2.685	1.539	-	-
4. DINA +	4	8	4	8	4	4	-	2	-	-	-
5. EDNA (Haleite)	2	6	4	4	2	2	-	2	1	-	-
6. Ednatol (60/40)	5.078	8.190	5.315	6.635	1.557	5.078	-	2.658	2.538	-	-
7. Pivonite	9	12	4	13	4	9	-	2	2	-	-
8. Hydrazine Nitrate +	-	5	3	3	2.5	-	-	1.5	-	0.25	-
9. NENO +	6	8	6	12	4	4	2	3	-	-	-
10. Nitroglycerine +	3	5	3	9	2.5	-	3	1.5	-	0.25	-
11. Nitroguanidine	1	4	4	2	1	1	-	2	1	-	-
12. Pentolite	5.825	5.91	3.23	8.04	2.215	5.825	-	1.615	0.74	-	-
13. PETN +	5	8	4	12	4	2	3	2	-	-	-
14. Picratol (50/50)	6.895	5.795	3.68	6.853	-	6.853	-	1.840	2.898	-	0.042
15. Picric Acid		3	3	7	1	6	-	1.50	0.5	-	-
16. RDX +	3	6	6	6	3	3	-	3	-	-	-
17. Tetryl	7	5	5	8	1	7	-	2.5	1.5	-	-
18. Tetrytol (70/30)	6.573	4.696	4.036	6.853	0.280	6.573	-	2.018	2.068	-	-
19. Tetrytol (60/40)	6.734	4.811	3.931	6.819	0.085	6.734	-	1.966	2.320	-	-
20. TNT	7	5	3	6	-	6	-	1.5	2.5	-	1
21. Lead Azide +	$[Pb(N_3)_2]$				$[Pb + 3N_2]$						
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)

* Calculations made for two values of HFE; see paragraph 9.

\+ Entry numbers 4, 8, 9, 10, 13, 16, 21 have same decomposition products for both arbitrary decomposition equations.

M_o	n_g	η	Q ($M_o$cal)	Q (cal/gm)	HFE	$A \cdot 10^3$	$B \cdot 10^6$	$k_{obs.}$	$\bar{k}$	h	
246.16	11	0	130.36	0.529	95.04	63.45	3.95	3100	282	12.6	1
250	12.415	0	226.71	0.907	- 8.97	71.21	4.56	3080	248	12.3	2
250	10.914	0	243.81	0.975	- 8.64	64.00	4.17	2950	270	11.8	3
240.16	10	0	*244.42 267.01	1.018 1.111	100 77.5	63.16	4.74	3100* 3000	305	12.9 12.5	4
150.12	7	0	149.25	0.994	24.2	42.28	3.02	1880	268	12.5	5
250	11.831	0	203.43	0.813	29.90	68.49	4.414	3000	254	12.0	6
384.25	17	0	*329.88 310.31	0.858 0.808	153 172.57	102.30	6.95	4500* 4550	266	11.7 11.8	7
95.08	4.25	0	87.03	0.915	60	27.80	2.30	1330	313	14.0	8
356.20	13	0	*433.41 403.00	1.217 1.132	101.8 132.2	89.44	5.95	4380* 4550	343	12.3 12.8	9
227.11	7.25	0	349.47	1.539	82.7	58.70	3.56	2915	402	12.8	10
104.09	5	0	69.62	0.668	18	29.33	2.02	1380	276	13.25	11
250	10.395	0	234.82	0.940	55.75	62.57	4.211	2950	284	11.8	12
316.17	11	0	451.79	1.429	123	82.42	5.34	3955	360	12.5	13
250	11.591	0.002	135.48	0.542	55.37	65.07	3.761	3010	260	12.0	14
229.2	9	0	170.71	0.745	53.5	53.08	3.35	2850	317	12.4	15
222.15	9	0	280.58	1.263	-21.3	55.89	4.11	2780	309	12.5	16
287.25	12	0	262.18	0.913	- 9.3	69.60	4.325	3450	288	12.0	17
250	10.939	0	200.52	0.802	- 1.4	62.09	3.683	2890	264	11.6	18
250	11.105	0	193.17	0.773	- 0.9	62.62	3.656	2900	261	11.6	19
227.16	10	0.053	154.00	0.678	13	60.51	3.435	2520	252	11.7	20
291.27	3	0.712	113.00	0.388	-111	23.10	1.11	990	330	11.8	21
(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	

TABLE IIA. Detonation Parameters - H_2O Arbitrary Decomposition Equation

	$\rho_o = 0.8$					$\rho_o = 1.0$				
Explosive	$D_{exp.}$	$D_{calc.}$	T_D	p_D	x_D	$D_{exp.}$	$D_{calc.}$	T_D	p_D	x_D
1. **Ammonium Picrate**						4990	4950	2700	62	2.22
2. **Composition A.**						5780	5750	3700	84	2.16
3. **Composition B.**						5690	5580	3770	82	2.09
4. **DINA***		5000	3370	55	1.87	5950	5770	3290	84	2.29
5. **EDNA (Haleite)**						5910	5870	3500	87	2.23
6. **Ednatol**	4850	4730	3500	50	1.73	5515	5460	3450	77	2.12
7. **Fivonite**						5215	5280	3290	74	2.09
8. **Hydrazine Nitrate***	4940	5140	2790	57	2.11	5830	5940	2670	89	2.61
9. **NENO***	4790	4880	4150	55	1.72	5530	5550	4040	83	2.11
10. **Nitroglycerine***										
11. **Nitroguandine**		4710	3000	48	1.88	5460	5470	2900	74	2.32
12. **Pentolite**	4860	4740	3600	51	1.72	5480	5430	3500	78	2.11
13. **PETN***	4760	5030	4580	57	1.70	5550	5700	4500	87	2.09
14. **Picratol**	4385	4310	3090	41	1.72	5020	4960	3010	63	2.11
15. **Picric Acid**	4645	4540	3190	46	1.82	5255	5210	3090	70	2.24
16. **RDX***		5170	4180	62	1.73	6080	5960	4070	95	2.12
17. **Tetryl**						5600	5510	3710	79	2.11
18. **Tetrytol (70/30)**						5250	5240	3590	72	2.05
19. **Tetrytol (60/40)**						5190	5220	3570	71	2.04
20. **TNT**	4360	4340	3380	41	1.63	5010	5000	3290	64	2.02
	$\rho_o = 2.0$					$\rho_o = 2.5$				
21. **Lead Azide***		2700	4480	39	1.38		3165	4300	62	1.73

* Entry Numbers 4, 8, 9, 10, 13, 16, 21 have same decomposition products for both arbitrary decomposition equations.

$\rho_0 = 1.2$					$\rho_0 = 1.4$					$\rho_0 = 1.6$					
$D_{exp.}$	$D_{calc.}$	T_D	P_D	x_D	$D_{exp.}$	$D_{calc.}$	T_D	P_D	x_D	$D_{exp.}$	$D_{calc.}$	T_D	P_D	x_D	
5680	5620	2620	91	2.63	6370	6300	2480	127	3.06	7050	6970	2340	175	3.54	1
6585	6500	3600	122	2.54	7390	7330	3450	171	2.96	8180	8260	3320	237	3.40	2
6310	6280	3640	117	2.48	6925	7020	3500	162	2.89	7540	7830	3330	220	3.29	3
6540	6520	3150	125	2.72	7125	7270	2970	174	3.18	7720	8130	2770	236	3.67	4
6565	6650	3360	128	2.66	7220	7430	3240	180	3.09						5
6180	6190	3340	112	2.54	6850	6930	3210	157	2.95	7510	7760	3060	214	3.37	6
5895	5950	3190	106	2.48	6580	6670	3050	147	2.89	7260	7460	2910	199	3.29	7
6720	6800	2500	130	3.11	7610	7700	2320	177	3.64	8500	8560	2120	253	4.19	8
6265	6280	3940	123	2.52	7000	7020	3780	166	2.91	7735	7800	3600	225	3.31	9
										8000	7990	4400	241	3.30	10
6260	6230	2800	109	2.76	7065	7040	2680	154	3.21						11
6100	6130	3370	114	2.52	6725	6860	3220	160	2.92	7340	7600	3080	213	3.34	12
6340	6430	4370	127	2.48	7130	7180	4230	176	2.89	7920	7950	4050	240	3.29	13
5655	5640	2920	92	2.52	6285	6300	2810	128	2.92	6920	7010	2690	175	3.33	14
5870	5900	2960	101	2.65	6480	6600	2780	140	3.09	7080	7300	2600	190	3.56	15
6805	6740	3930	137	2.54	7520	7500	3760	188	2.95	8235	8300	3570	255	3.37	16
6250	6205	3590	115	2.52	6895	6920	3440	160	2.92	7535	7700	3280	213	3.33	17
5930	5940	3500	96	2.42	6605	6650	3370	144	2.82	7280	7390	3220	196	3.23	18
5880	5900	3480	103	2.41	6575	6600	3350	142	2.80	7255	7350	3210	192	3.19	19
5655	5680	3200	93	2.40	6300	6360	3110	128	2.78	6940	7030	3010	174	3.16	20
$\rho_0 = 3.0$					$\rho_0 = 3.5$					$\rho_0 = 4.0$					
	3760	4280	95	2.15		4465	4150	140	2.64		5300	3970	209	3.21	21

TABLE IIB. Detonation Parameters - CO Arbitrary Decomposition Equation

	$\rho_o = 0.8$					$\rho_o = 1.0$				
Explosive	$D_{exp.}$	$D_{calc.}$	T_D	p_D	x_D	$D_{exp.}$	$D_{calc.}$	T_D	p_D	x_D
1. Ammonium Picrate						4990	4990	2000	65	2.52
2. Composition A.						5780	5810	2855	89	2.27
3. Composition B.						5690	5600	3350	83	2.10
4. DINA ✦ *HFE = 100 HFE = 77.5		5000 5040	3370 3645	55 57	1.87 1.77	5950	5770 5790	3290 3540	84 88	2.29 2.18
5. EDNA (Haleite)						5910	5850	3060	89	2.28
6. Ednatol	4850	4825	2813	51	1.83	5515	5500	2720	79	2.25
7. Fivonite* HFE = 153 HFE = 172.57						5215	5320 5260	2920 2770	72 71	2.18 2.20
8. Hydrazine Nitrate ✦	4940	5140	2790	57	2.11	5830	5940	2670	89	.2.61
9. NENO ✦* HFE = 101.8 HFE = 132.2	4790	4880 4875	4150 3910	55 55	1.72 1.81	5530	5550 5610	4040 3800	83 84	2.11 2.20
10. Nitroglycerine ✦	-	-	-	-	-	-	-	-	-	-
11. Nitroguanidine		4790	2295	50	2.07	5460	5555	2164	77	2.57
12. Pentolite	4860	4755	3390	54	1.78	5480	5400	3280	81	2.13
13. PETN ✦	4760	5030	4580	57	1.70	5550	5700	4500	87	2.09
14. Picratol	4385	4300	2130	40	1.95	5020	4950	2010	62	2.39
15. Picric Acid	4645	4570	2997	46	1.87	5255	5240	2875	70	2.29
16. RDX ✦		5170	4180	62	1.73	6080	5960	4070	95	2.12
17. Tetryl						5600	5490	3310	82	2.15
18. Tetrytol (70/30)						5250	5290	2950	75	2.13
19. Tetrytol (60/40)						5190	5270	2840	73	2.15
20. TNT Diamond Volume used for Solid Carbon	4360	4315	2540	42	1.77	5010	4970	2450	65	2.15
	$\rho_o = 2.0$					$\rho_o = 2.5$				
21. Lead Azide ✦		2700	4480	39	1.38		3165	4300	62	1.73

* Calculations made for two values of HFE; see paragraph 9.

✦ Entry Numbers 4, 8, 9, 10, 13, 16, 21 have same decomposition products for both arbitrary decomposition equations.

ρ_0 = 1.2					ρ_0 = 1.4					ρ_0 = 1.6					
$D_{exp.}$	$D_{calc.}$	T_D	P_D	x_D	$D_{exp.}$	$D_{calc.}$	T_D	P_D	x_D	$D_{exp.}$	$D_{calc.}$	T_D	P_D	x_D	
5680	5665	1822	93	3.02	6370	6360	1620	129	3.56	7050	7070	1485	179	4.13	1
6585	6555	2704	127	2.70	7390	7300	2550	174	3.17	8180	8130	2333	232	3.65	2
6310	6280	3200	118	2.50	6925	6990	3050	161	2.91	7540	7730	2865	219	3.35	3
6540	6520 6525	3150 3395	125 127	2.72 2.61	7125	7290 7300	2970 3250	174 175	3.18 3.03	7720	8130 8085	2770 3055	236 239	3.67 3.47	4
6565	6610	2930	129	2.71	7220	7410	2750	178	3.16						5
6180	6200	2574	113	2.67	6850	6905	2625	154	3.13	7510	7660	2234	207	3.59	6
5895	5975 5940	2776 2620	107 100	2.58 2.61	6580	6670 6650	2610 2490	144 141	3.02 3.05	7260	7430 7385	2469 2305	200 196	3.47 3.51	7
6720	6800	2500	130	3.11	7610	7700	2320	177	3.64	8500	8560	2120	253	4.19	8
6265	6280 6335	3940 3660	122 120	2.52 2.62	7000	7020 7100	3780 3500	166 167	2.91 3.05	7735	7800 7900	3600 3310	225 228	3.31 3.48	9
–	–	–	–	–	–	–	–	–	–	8000	7990	4400	241	3.30	10
6260	6305	2015	109	3.09	7065	7110	1835	148	3.65						11
6100	6095	3158	114	2.51	6725	6770	3010	155	2.93	7340	7530	2835	207	3.36	12
6340	6430	4370	127	2.48	7130	7180	4230	170	2.89	7920	7950	4050	240	3.29	13
5655	5610	1878	89	2.86	6285	6290	1725	122	3.36	6920	7000	1558	163	3.90	14
5870	5915	2728	102	2.73	6480	6620	2565	141	3.20	7080	7310	2382	194	3.67	15
6805	6940	3930	137	2.54	7520	7500	3760	188	2.95	8235	8300	3570	255	3.37	16
6250	6190	3172	117	2.56	6895	6900	3000	159	2.98	7535	7665	2818	211	3.41	17
5930	5940	2820	106	2.53	6605	6610	2670	145	2.96	7280	7310	2495	195	3.39	18
5880	5930	2710	104	2.56	6575	6600	2550	144	2.99	7255	7300	2385	193	3.44	19
5655	5610	2335	92	2.56	6300	6290	2200	128	3.00	6940	7015	2040	172	3.47	20
ρ_0 = 3.0					ρ_0 = 3.5					ρ_0 = 4.0					
	3760	4280	95	2.15		4465	4150	140	2.64		5300	3970	209	3.21	21

Table III Values of $\Sigma n_i k_i$ calculated with various sets of species covolume factors, k_i

EXPLOSIVE	H_2O Arbitrary Decomp. Equation ($\delta = k_{obs.} - \Sigma n_i k_i$)					CO Arbitrary Decomp. Equation ($\delta = k_{obs.} - \Sigma n_i k_i$)				
	(1) $k_{obs.}$	(2) $k_i I$*	(3) δ	(4) $k_i II$*	(5) δ	(6) $k_{obs.}$	(7) $k_i III$*	(8) δ	(9) $k_i IV$*	(10) δ
1. Ammonium Picrate	2790	2781	9	2790	0	3100	2943	157	2950	150
2. Composition A	2875	2818	56	2830	44	3080	3078	2	3097	- 17
3. Composition B	2890	2942	- 52	2915	- 25	2950	3071	-121	3037	- 87
4. DINA	3100	3030	70	3080	20	3050	3012	38	3056	- 6
5. EDNA	1825	1839	- 15	1845	- 21	1880	1916	- 36	1922	- 42
6. Ednatol	2835	2851	- 17	2865	- 31	3000	3055	- 55	3072	- 72
7. Fivonite	4315	4470	-155	4605	-290	4525	4602	- 77	4741	-216
8. Hydrazine Nitrate	1330	1303	27	1302	28	1330	1298	32	1294	36
9. NENO	4380	4473	- 92	4450	- 69	4465	4480	- 15	4452	13
10. Nitroglycerine	2915	2884	31	2863	52	2915	2900	15	2888	27
11. Nitroguanidine	1260	1276	- 16	1240	20	1380	1363	17	1325	55
12. Pentolite	2945	2961	- 16	2992	- 47	2950	3012	- 62	3036	- 86
13. PETN	3955	3983	- 28	4010	- 55	3955	3986	- 31	4023	- 68
14. Picratol	2685	2679	5	2693	- 9	3010	2917	93	2933	77
15. Picric Acid	2790	2684	104	2662	126	2850	2728	122	2693	157
16. RDX	2780	2856	- 76	2805	- 25	2780	2859	- 79	2793	- 13
17. Tetryl	3370	3322	48	3282	88	3450	3452	- 2	3400	50
18. Tetrytol (70/30)	2770	2784	- 14	2766	4	2890	2959	- 69	2935	- 45
19. Tetrytol (60/40)	2730	2750	- 18	2737	- 5	2900	2944	- 44	2928	- 28
20. TNT	2320	2305	13	2322	- 4	2520	2509	11	2529	- 9
21. Lead Azide	990	1170	-180	990	0	990	1200	-210	1002	- 12

* $k_i I$ and $k_i III$ were obtained with $Pb(N_3)_2$ omitted. $k_i II$ and $k_i IV$ with $Pb(N_3)_2$ included, see Section 4.

TABLE IV
Thermodynamic Constants

i	HF_i	$A_i \cdot 10^3$	$B_i \cdot 10^6$
H_2	0	5.02	0.28
CO_2	94.45	10.30	0.42
CO	26.84	5.82	0.33
H_2O	57.80	7.13	0.67
N_2	0	5.68	0.37
C	0	4.52	0.20

Calculations of heat capacities which were recently carried out at this laboratory (see ref. 11) showed the above values of A and B for CO and N_2 to be somewhat in error. Detonation velocities for lead azide (which, of all explosives considered here, is most affected) recalculated with the new heat values of reference 11, were not appreciably different from those reported; they were higher than the curve shown on Fig. 20 by ~ 2% at the lower densities and $< 1.5\%$ at the higher densities.

List of References

1. The Properties of Gases at High Pressures which can be Deduced from Explosion Experiments. H. Jones. Third Symposium on Combustion, Flame and Explosion Phenomena. The Williams and Wilkins Co. 1949.
2. Final Report on The Hydrodynamic Theory of Detonation and Shock Waves. G B. Kistiakowsky and E. Bright Wilson, Jr. Division B, NDRC, OSRD Report No. 114. June 30, 1941.
3. Report on Revised Method of Predicting the Detonation Velocities in Solid Explosives. S. R. Brinkley, Jr. and E. B. Wilson, Jr. Division B, NDRC, OSRD Report No. 905. Sept. 28, 1942.
4 Progress Report on Calculation of the Detonation Velocities of Some Pure Explosives. S. R. Brinkley, Jr. and E. B. Wilson, Jr. Division 8, NDRC, OSRD Report No. 1707. August 12, 1943.
5. The Compression of 39 Substances to 100,000 KG/CM^2. P W Bridgman. Proc Am. Acad. Arts Sci. 76,55 (1948).
6. On the Calculation of Detonation Velocities. H. G. Snay. NAVORD 1860 (to be published).
7. The Rate of Detonation of Various Explosive Compounds and Mixtures. Explosives Research Laboratory, Division 8, NDRC, OSRD Report No. 5611. Jan. 15, 1946.
8. The Hydrodynamic Theory of Detonation. Part II. On Absolute Calculations for Condensed Explosives. Stewart Paterson. Research (London) 1, 221 (1948).
9. Thermochemische Tabellen fur die Explosivchemie. A. Schmidt. Zeitschrift fur das gesamte Schiess- und Sprengstoffwesen, Vol. 29, Nos. 9 and 10. September and October 1934, pp 259-266 and 296-301.
10. Heat of Combustion of Explosive Substances. Gebhard Stegeman. Division 8, NDRC, OSRD Report No. 5306. July 4, 1945.
11. Heat Capacities for Calculations of Explosion Phenomena. M. J. Fischer and H. G. Snay. NAVORD 1804 (to be published).
12. Tables, Forms and Graphs for Calculations of Shockwave and Detonation Phenomena B. A. Cotter, M. J. Fischer and H.G. Snay. NAVORD 1859. (to be published).

DISTRIBUTION LIST

		Copies
Chief, Bureau of Ordnance	Attn: Ad3	2
	Attn: Ad6	1
	Attn: Re06	1
Armed Services Technical Information Agency, Document Service Center, Knott Building, Dayton 2, Ohio		5

UNCLASSIFIED

AD 116872

Armed Services Technical Information Agency

Reproduced by

DOCUMENT SERVICE CENTER

KNOTT BUILDING, DAYTON, 2, OHIO

UNCLASSIFIED