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Report on "The Prediction of Detonation Velocities
of Solid Explosives"

OD-02

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of NNDG List No. 4

Dated - Mar 25-29, 1946

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OF THE
Dated Mar. 25-29, 1946

Section A-1

Report on "The Prediction of Detonation Velocities
of Solid Explosives."
(OD-02)

Endorsement (1) from G. B. Kistiakowsky, Member Section A-1, to T. L. Davis, Chairman, Section A-1. Forwarding report.

(2) From T. L. Davis, Chairman, Section A-1, to J. B. Conant, Chairman, Division B. Forwarding report and noting:

"The report appears to solve the problem of predicting in advance of experiment, the velocity of detonation of an explosive substance, if its heat of combustion and density are known - with an accuracy equal to the average experimental determination. This result seems to me to be of the greatest scientific importance, and it is hoped that the substance of this report may ultimately be published where it will be available to scientists, and where full credit may be given to Professors Kistiakowsky and Wilson."

(3) Five copies forwarded to Dr. Irvin Stewart, Secretary of the National Defense Research Committee, as Progress Report under contract in which G. B. Kistiakowsky and E. Bright Wilson (#35) are Official Investigators, Division B, Serial No. 6.

"Special attention directed to the second endorsement. The work of the explosives section will be in large manner directed along lines of research suggested by this method of prediction, using heats of combustion and additional observations to check theory being obtained as part of NDRC program."

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J. B. Conant, Chairman

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Serial
~~Technical Report~~ No. 6

Section A-1

Explosives

Declassified by authority
of ~~XXXXX~~ 14
Dated Mar. 25-29, 1946

Report on
The Prediction of Detonation Velocities of Solid Explosives

by

Professors G. B. Kistiakowsky and E. B. Wilson, Jr.

Harvard University

Division B

National Defense Research Committee

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The Hydrodynamic Theory of Detonation Waves

Part II. The Prediction of Detonation
Velocities for Solid ExplosivesDeclassified by authority
of E.O. 13526, List No. 14
Dated Mar. 25-29, 1996

Summary

The hydrodynamic theory of Part I should permit the calculation of the detonation velocity of an explosive if the following information were available: composition, heat of formation, density, and equation of state of the products. Unfortunately no completely satisfactory a priori equation of state data are available for these high temperatures and pressures. However, an approximate form of the equation of state (Becker) is available containing one unknown constant (which is a function of the composition of the products, and of the temperature, but is independent of pressure). This constant is of the nature of covolume. If this covolume could be calculated for a given composition of the products, the detonation velocity of a new explosive could then be obtained using only known or readily obtainable data, in most cases.

In this investigation the covolumes were obtained by working backward from the measured detonation velocities at varying densities of loading for a considerable number of explosives. These results (given in Table 4, where k_T is the covolume in question) show first that k_T does not vary much with density of loading, which confirms the assumption that the form of the equation of state used is approximately correct. Secondly, the covolumes obtained in this way can be expressed as a simple function of the composition, namely as an additive function of

the covolumes of the constituent molecules of the product. The values assigned to the covolumes of the individual species were adjusted empirically so that the covolumes of the mixtures agreed with those found as above and listed in Table 6. Actually for most of the organic explosives only four different covolumes occur so that this whole procedure amounts essentially to fitting the observed detonation velocities to a formula which involves the heat of formation, the density, the chemical composition and four empirical constants. Furthermore these constants agree surprisingly well with the van der Waals covolumes, when reduced to the same temperature.

Having succeeded in reducing a considerable body of data in this way, it becomes possible to reverse the process. The empirical species-covolumes obtained above may be used to calculate detonation velocities for new explosives as yet unmeasured. Furthermore, this calculation can be carried out approximately for substances which have not been prepared at all, because the necessary heat of formation and density can be estimated from the properties of related compounds and from various additivity rules, etc.

The results described above are tabulated in Tables 4, 5, and 6. The text of this report discusses the method of calculation and the nature and effect of the approximations and assumptions used. Appendix II gives in concise practical form the procedure for carrying out the numerical calculations in any given case.

Introduction

In a preliminary report under the same title (hereafter referred to as Part I), the authors discussed the general theory of detonation and shock waves as developed by Hugoniot, Raleigh, Jouguet, Becker and others. The present report gives an account of the theoretical work done by Dr. R. S. Halford in cooperation with us in an attempt to develop theoretically rigorous and yet practically useful equations from which the detonation rate (and incidentally the pressure and temperature in the detonation wave) could be calculated for any explosive. The only data which the theory requires from experiment are the composition, heat of formation, and density of the explosive.

This goal has not been quite reached as yet but none-the-less the present form of the detailed theory enables one to calculate the detonation rate of most explosives (i.e. all organic materials and some others) with very few ad hoc assumptions and with an accuracy that compares favorably with the accuracy of experimental measurements of this quantity. The prediction of the detonation rates of new compounds becomes therefore possible and if the accuracy desired is not too great, this can be done without any experimental work at all, because the heats of formation and the densities can be estimated from comparison with known analogous compounds. Each calculation involves not more than 20-30 minutes of arithmetical work and hence may be strongly recommended to all who intend to synthesize new compounds.

At the end of the report we have appended a brief statement of the procedure to be followed in calculating the detonation

velocity of a new compound. This is intended for those who do not want to read through the rather extensive mathematical operations of the main body of the report.

Certain limitations of the theory must be stressed now. The theory gives only the greatest possible detonation velocity under given conditions of loading and hence presumably the maximum brisance. Whenever the initiation of detonation has been inadequate and detonation is chemically incomplete, less vigorous action must be expected. No information as to the ease of initiation, that is the sensitivity of the explosive, is to be gained from the theory. Finally, the theory breaks down when one of the products is partially gaseous and partially solid or liquid under the conditions existing in the detonation wave. Only when each product is present substantially quantitatively in one phase will the theory give a correct result.

1. General theory applied to solid explosives

In Part I the following general equations were derived:

$$\rho_1 D = \rho_2 (D-w) \quad (1)$$

$$P_2 - P_1 = \rho_1 D^2 - \rho_2 (D-w)^2 \quad (2)$$

$$E_1 + \frac{1}{2} D^2 + \frac{P_1}{\rho_1} = E_2 + \frac{1}{2} (D-w)^2 + \frac{P_2}{\rho_2} \quad (3)$$

where D and w denote the detonation velocity and the material velocity in the wave respectively, the subscripts 1 and 2 denote quantities relating to the state before the passage of the wave and to the state existing immediately behind the crest

of the wave, P is the pressure, ρ the density and E the energy (thermal and chemical) per gram of material. The following equation defining the detonation velocity was also obtained in Part I (see Eq. I-5-6 and I-5-7):

$$D = v_1 M^{-1/2} \left(- \frac{dP_2}{dv_2} \right)_S^{1/2} \quad (4)$$

The derivative is to be taken adiabatically and reversibly. v_1 and v_2 are the volumes occupied by M grams (for instance 1 mole) of the explosive before the passage of the wave and by the detonation products derived from M grams in the wave. It is assumed that the chemical reactions have been completed by the time the crest of the wave reached a given spot in the explosive.

In solid explosives the initial pressure is of the order of one atmosphere whereas P_2 is 10^5 Atm. and greater; v_2 on the other hand is only slightly smaller than v_1 and therefore P_1 and $P_1 v_1$ will be neglected in the following compared with P_2 or $P_2 v_2$. The resultant error is wholly negligible but the simplification is great because the equation of state of the explosive before detonation is eliminated from consideration. For the gaseous products of detonation the following rather general equation of state will be introduced now:

$$P_2 = \frac{nR T_2}{f(v_2, T_2)} \quad (5)$$

where $f(v_2, T_2)$ is an unspecified function of the volume of M grams and of temperature and n is the number of moles of gaseous products formed from M grams of the explosive. The function, f , is also a function of the mole number n . In general n will change

with T and P because of shifts in the various equilibria, thus causing f to depend implicitly on T and v through n as well as explicitly on T and v. In what follows this implicit dependence will be ignored, i.e. n treated as a constant. The more general treatment introduces but slight gain in accuracy as will be seen and produces great complication.

Substituting the equation of state (5) into the well-known thermodynamic relation:

$$\left(\frac{\partial P}{\partial v}\right)_s = \frac{C_p}{C_v} \left(\frac{\partial P}{\partial v}\right)_T = \gamma \left(\frac{\partial P}{\partial v}\right)_T \quad (6)$$

one obtains for the velocity of detonation the new expression:

$$D = \frac{v_1}{f(v_2, T_2)} \left(\gamma f'(v_2) \frac{nR T_2}{M} \right)^{1/2} \quad (7)$$

where $f'(v)$ stands for the partial: $\left(\frac{\partial f(v, T)}{\partial v}\right)_T$. The quantities w , P_2 and D are now eliminated from equations (2) and (3) giving the following expressions:

$$\frac{C_p}{C_v} = \gamma = \frac{f(v_2, T_2)}{(v_1 - v_2) f'(v_2)}, \quad (8)$$

$$M(E_2 - E_1) = \frac{nR T_2}{2 \gamma f'(v_2)}. \quad (9)$$

Here C stands for the true heat capacity of the gaseous mixtures under the conditions of the detonation wave. The energy change in equation (9) may be replaced by the following expression derived from the First Law of Thermodynamics:

$$M(E_2 - E_1) = Q_{v_2} + N(T_2 - T_1) \bar{C}_{v_i} + M \int_{v_1}^{v_2} \left(\frac{\partial E}{\partial v}\right)_{T_2} dv \quad (10)$$

where Q_v is the heat absorbed (Q is positive when heat is absorbed) in the reaction of M grams of reactant to give the assumed composition of products and is measured in a constant volume calorimeter at the temperature of the explosive (T_1 , normally the room temperature). \bar{C}_{v1} is the mean heat capacity (from T_1 to T_2) of M grams of the product mixture divided by the total number of moles, N (in the ideal gas state or as solids or liquids at low pressures). The coefficient $(dE/dv)_{T_2}$ must be evaluated from the equation of state of the product mixture using conveniently the relation:

$$M \left(\frac{\partial E}{\partial v} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_v - P. \quad (11)$$

Until now the calculation has been carried out rigorously, but the results are too cumbersome for practical use.

Extensive studies have revealed that a very convenient method for the solution of the problem is to attack it in two steps. The first neglects gas imperfections and introduces certain other simplifications, while the second either eliminates these approximations or demonstrates their unimportance for the final result.

2. Calculation of "ideal" detonation velocity

Replacement of the equation of state (5) by $P_1 v = n_1 R T_1$ where n_1 is the number of moles of gaseous products leads immediately to the following simplification of equations given previously: (the subscript 1 refers to the "ideal" state)

$$\frac{v_2}{v_1 - v_2} = \frac{C_{P1}}{C_{v1}} = \gamma_1, \quad (12)$$

$$-Q_v = N_1 (T_2 - T_1) \bar{C}_{v1} - \frac{n_1 R T_{21}}{2 \gamma_1}, \quad (13)$$

$$D_1 = \frac{v_1}{v_2} \left(\gamma_1 \frac{n_1 R T_{21}}{M} \right)^{1/2}. \quad (14)$$

From these equations the detonation velocity D_1 is readily calculated when the composition of the product mixture is known. The heats of reaction are calculated by the First Law from the heats of formation or combustion, available for many compounds in tabular form. Heat capacities of most simple molecules have been calculated statistically to very high temperatures by many authors and in Table 7 are given energy integrals derived from such data in analytical form accurate to about 1% over the temperature range 2000 to 5000°K.

Since calculations of this section are concerned with an "ideal" state, its definition is arbitrary and will be chosen so as to provide the greatest convenience in calculations and yet to facilitate the subsequent problem of calculating true detonation rates. For this purpose the following assumptions are made:

- (1) All product gases are ideal and the volume of solid or liquid products may be neglected.
- (2) All dissociations into free radicals and atoms are non-existent.
- (3) Only solid carbon, CO, CO₂, H₂O, H₂O₂, N₂ (and gaseous sulfur, SO₂, metals or metallic oxides, insofar as the corresponding elements are present in the explosive) are formed.
- (4) Oxygen reacts quantitatively with carbon to form CO, the excess forms quantitatively H₂O and what is left over reacts to form CO₂.

The question of whether a real pressure and temperature range exists in which all these assumptions hold is entirely immaterial for the following, because D_1 and other "ideal" quantities

resulting from these calculations are merely convenient steps to reach the real detonation rates.

In Appendix II of this report examples are given of the detailed procedure followed in the calculation of ideal quantities here defined.

3. The calculation of real detonation rates.

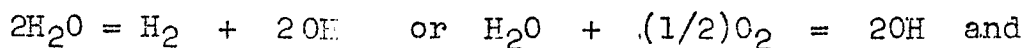
A rigorous calculation of true detonation rates cannot be carried out at present, a sufficient reason for this being that the equation of state of gaseous mixtures at densities above 1 g/cc and temperatures of over 5000°K is unknown.

In fact several approximations and simplifications and one frank assumption (the form of the equation of state) must be made and they will now be considered one by one.

Dissociation into atoms and free radicals is fortunately not of importance because of the high pressures in detonation waves of solid explosives at ordinary densities of loading. Consider for example the dissociation $H_2 = 2 H$. At 5000°K (rather high for most explosives) the dissociation constant has been calculated statistically to be 44.7 Atm. The concentration of free hydrogen does not exceed 10% by volume with most explosives and if the total pressure is 10^5 Atm. it is readily found that 2% of hydrogen is dissociated into atoms. This means an absorption of heat roughly equal to 3 Kcal per Kg of explosive, whose total heat of explosion is normally of the order of 1000 Kcal/Kg. Thus T_2 is lowered by the inclusion of this dissociation to the extent of 0.3% but at the same time the mole number is increased and hence the pressure is greater. This effect is of the order of

0.10% and hence the total effect on the detonation rate is (because of the square root relation) $(1/2)(0.3-0.10)\% = 0.10\%$.

Similar calculations show that the water dissociations:



$2\text{H}_2\text{O} = \text{O}_2 + 2\text{H}_2$ are of small importance. Dissociations of oxygen and nitrogen are still more insignificant.

Various polyatomic molecules have been reported in the gas samples withdrawn from bombs after detonation. Thus Schmidt (Part I) reports $\text{CH}_4, \text{C}_2\text{H}_2, \text{HCN}, \text{C}_2\text{N}_2, \text{NH}_3$ in variable but small amounts from almost all explosives. To allow for equilibrium formation of all these molecules seems mathematically an almost impossible task, particularly when it is considered that the thermodynamic functions of most of these molecules are not too accurately known at the high temperatures in question. Approximate calculations made on some of those which are found in greatest amounts indicate that the observed concentrations are in excess of equilibrium under the conditions of the detonation wave (thus with TNT Schmidt reports roughly equimolecular quantities of ammonia and hydrogen whereas the equilibrium ratio is less than 1:10). In all probability these molecules are formed during the cooling process after detonation. But even when it is supposed that the analytical data represent the true conditions in the detonation wave, the formation of all these complex molecules does not alter greatly the results of calculation.

Taking as an example the particularly unfavorable case of TNT for which the oxygen deficiency is large and the complex products particularly abundant according to Schmidt, one finds

that in the formation of all complex products reported by Schmidt a total of 8.7 Kcal of heat is absorbed per Kg. of TNT, while the total heat evolution is 875 Kcal. At the same time the mole number of gaseous products is reduced from 32.6 to 30.7 and therefore the total effect on the detonation rate is approximately $[(30.7/32.6)(875/866.3)]^{(1/2)} = 0.965$. The neglect of the complex products thus overestimates the rate by 3.5%, but it is believed that in general the corresponding error is smaller.

The formation of free hydrogen in the detonation wave in the absence of solid carbon can be neglected because the equilibrium constant of the reaction $H_2O + CO = CO_2 + H_2$ ranges from 0.2 at 3000° to 0.07 at $5000^\circ K$. Thus the greater part of the hydrogen is present as water and the formation of a few moles of free hydrogen per Kg of explosive is of little effect on the detonation rate. This follows because there is no mole number change in the reaction and the heat evolution is only 4.5 Kcal. per mole at 3000° and is less at 5000° . The neglect of hydrogen in the absence of solid carbon causes therefore an underestimation of the rate by a few percent at most.

In the presence of free carbon, on the other hand, the formation of free hydrogen will proceed almost quantitatively. The equilibrium constant of the reaction $C + H_2O = CO + H_2$ is about 10^5 Atm. at $3000^\circ K$ and may be estimated as 5×10^6 Atm. at 5000° . Since the pressure (or fugacity, to be more correct) of carbon monoxide in the detonation wave seldom rises to 10^5 Atm., the ratio P_{H_2}/P_{H_2O} is greater than unity so long as carbon is present. The assumption that the reaction goes completely to the right means

an overestimation of the detonation rate because the heat absorption is overcompensated by an increased mole number of gaseous products. The following examples in Table I demonstrate the magnitude of the effect on D of the extreme assumptions concerning this equilibrium. It is seen that ideal rates calculated with no carbon and those calculated with no hydrogen differ only by 3% or less. In actuality the first case is approached closely almost always and hence the error resulting from the extreme assumption must be small.

Table I
Effect of equilibria on ideal detonation rates.

Compound	Decomposition equation	T_i °K	D_i m/sec.
Picric Acid	$6 \text{ CO} + \text{H}_2\text{O} + \frac{1}{2} \text{H}_2 + 1\frac{1}{2} \text{N}_2$	3440	2140
	$5\frac{1}{2} \text{CO} + 1\frac{1}{2} \text{H}_2\text{O} + \frac{1}{2} \text{C} + 1\frac{1}{2} \text{N}_2$	3615	2120
TNT	$6 \text{ CO} + 2\frac{1}{2} \text{H}_2 + \text{C} + 1\frac{1}{2} \text{N}_2$	2880	2070
	$3\frac{1}{2} \text{CO} + 2\frac{1}{2} \text{H}_2\text{O} + 3\frac{1}{2} \text{C} + 1\frac{1}{2} \text{N}_2$	3650	2005
Tetryl	$7 \text{ CO} + \text{H}_2\text{O} + 1\frac{1}{2} \text{H}_2 + 2\frac{1}{2} \text{N}_2$	3950	2360
	$5\frac{1}{2} \text{CO} + 2\frac{1}{2} \text{H}_2\text{O} + 1\frac{1}{2} \text{C} + 2\frac{1}{2} \text{N}_2$	4245	2290

Summing up the results of this discussion it is found that the effects of chemical equilibria in the detonation wave are divers and altogether may effect a decrease of the rate with increasing pressure (or density of loading) amounting to perhaps 10 or at the very most 15%. This conclusion is interesting from the theoretical point of view since it indicates that the study of

detonation rates does not provide strong evidence as to whether chemical equilibria are established in the wave or not. For the detonation to comply with the present theory it is only necessary to postulate that the reaction is "complete" in the sense that the oxygen combines with all the carbon to form CO, the excess oxygen combines with hydrogen to form water and if any is still left over, it combines with CO to form CO₂.

Experimental evidence shows that, with increasing density of the explosive, the detonation rates rise sharply and reach values almost four times as high as the "ideal" values calculated by the described procedure. Other simplifications having been now eliminated, it appears probable that the rise is due to deviations of gases from ideal behaviour, unless, of course, the whole theory is fundamentally incorrect. In Part I the calculations of Schmidt, who has made use of the Abel equation of state, have been reviewed to show that qualitatively at least deviations from ideal behaviour may be made to account for the observed rise.

However the Abel equation, as well as its parent the van der Waals equation of state, is specifically derived for gases at low densities and must fail under conditions encountered in the detonation waves. Bridgman has studied the behaviour of nitrogen at room temperature and at densities as high as 1.2 g/cc and has found that the semi-empirical equation of Becker describes his experimental observations very well. This equation has four arbitrary constants and is written by Bridgman in the form:

$$P = \frac{RT}{v} \left(1 + \frac{k}{v} e^{\frac{k}{v}} \right) - \frac{a}{v^2} + \frac{c}{v^{n+2}} \quad (15)$$

At the high densities of Bridgman's experiments, however, the last two terms are of minor significance. Omitting them and changing somewhat the value of the constant k - the only remaining arbitrary constant - one can obtain almost as good an agreement with Bridgman's data as he was able to obtain with four constants. (The second correction term, describing an attraction between molecules, must become quite unimportant at the high temperatures and densities of the detonation waves and the last term was used by Becker to obtain agreement at the critical point.) It was decided, therefore, to use the Becker equation in abridged form with only one adjustable constant. It is known from several experimental and theoretical sources, however, that the repulsive energy between molecules can be represented as proportional to the inverse ninth to twelfth power of the distance of approach. Now, with increasing temperature the kinetic energy of molecules increases linearly and hence they must approach closer on collisions. The constant k of the Becker equation which, as one can readily convince oneself, becomes equivalent to the van der Waals (or Abel) covolume in the limit of low densities and is therefore proportional to the cube of the molecular diameter, must be temperature dependent. Depending on which of the molecular repulsion laws is chosen, one must take either a $T^{-1/3}$ or $T^{-1/4}$ dependence of k . The former was actually chosen for the calculations, because it fortuitously shortens the algebraic labor, and the final form of the equation of state is: (where $k = K/T^{1/3}$)

$$P = \frac{nRT}{V} \left(1 + \frac{K}{vT^{1/3}} e^{\frac{K}{vT^{1/3}}} \right) \quad (16)$$

In the form in which the equation is written above, the term $KT^{-1/3}$ is the covolume of all the molecules formed from M grams of the reactant. As the following will show, it may be represented as a summation over the individual covolumes of the different products formed.

The substitution of equation (16) into the basic equations derived in Section 1 is laborious but straightforward. A few simplifications in minor terms had to be made, but all of them have been checked and found to alter the result insignificantly. The calculation is discussed in detail in the Appendix and here only the final results for the ratio D/D_1 and for the equivalent of equation (8) will be written

$$\left(\frac{D}{D_1}\right)^2 = \left(\frac{1+2xe^x+x^2e^x}{\bar{n}_i} \left(\frac{1}{\left[1 + \frac{R}{2\bar{c}_{v1}} \left\{ 1 - \frac{(1+xe^x)^2}{\left(\frac{R}{\bar{n}_i}\right)(1+2xe^x+x^2e^x)} \right\} \right] \left[1 + \frac{Rxe^x}{3\bar{c}_{v1}}\right]} \right) \right)^2 \cdot \left(1 + \frac{\frac{R}{9\bar{c}_{v1}} (3+2xe^x-x^2e^x)^2}{\left[1 + \frac{R}{9\bar{c}_{v1}} (2xe^x-x^2e^x)\right] \left[1+2xe^x+x^2e^x\right]} \right)^2 \right) \quad (17)$$

$$\frac{k\bar{e}_i}{MT^{-1/3}} = \frac{k}{M} \bar{e}_i = \frac{x}{1 + \frac{1+xe^x}{\bar{n}_i \left(\frac{R}{\bar{n}_i}\right) (1+2xe^x+x^2e^x)}} \quad (18)$$

In these equations the variable x has been used to abbreviate $KT^{-1/3}/v_2$, while $\bar{c}'_{v1} = \bar{c}_{v1} - R/2\bar{n}_1$. Since equation (18) relates the quantity $k\bar{e}_i/M$ to x , the ratio D/D_1 may be calculated and plotted as the function of the former. In making this calcula-

tion it is found that the numerator of the first factor in equation (33) contributes by far the greatest variation in D/D_1 with density. The product of all the other factors makes at most 30% difference in the result. In equation (34) the effect of reasonable changes in the values of γ_1 and (γ/γ_i) is extremely small. This means that the actual values of the heat capacity of the product mixture are of very small import for the shape of the D/D_1 curve. In Table 2 three calculations have been made, the first for $C_{v1} = 11.5$, the second for $C_{v1} = 9$ and the third for $C_{v1} = 6.5$ cal/mole degree. All known explosives fall into this range of C_{v1} values and the variation between the three cases is so small that if no great accuracy were desired one could use a universal function for all explosives. In Table 3 we give the values of $k_T \rho_1/M$, (γ/γ_i) and T/T_1 . They depend only very slightly upon the value of C_{v1} chosen (the calculations have been made for $C_{v1} = 8$) and therefore the standard values of (γ/γ_i) were used for the second factor in equation (33). A further simplification in the calculations was the neglect of the dependence of k , C_{v1} and \bar{C}'_{v1} upon T as it varies with increasing density of the explosive. The corresponding changes are very small and so long as a consistent procedure is used for all explosives the damage to the results is entirely insignificant.

In Table 4 have been collected practically all published determinations of the detonation velocities of militarily interesting pure and mixed explosives. Only measurements on "safety" explosives have been excluded as these are usually made up of coarse particles of the combustible and the oxygen carrier, such inhomogeneity being deliberately resorted to in order to slow down

the detonation velocity below that demanded by the theory. For each explosive the ideal temperature and detonation velocity were calculated by the method outlined in Appendix II and the ratios D/D_1 formed using experimental data. Then that one of the three functions given in Table 2 was used, whose C_{v1} value was nearest to the calculated C_{v1} in the detonation wave; from it the values of k (ρ_1 / M) were read off for all experimental data. The corresponding k are then easily calculated and these are given in the 3rd column of the Table. The averages of the k for each explosive are also given; the deviations of individual values from such averages are rather large. It must be considered, however, that experimental values of both the detonation velocity and the bulk density enter into the calculation and in view of the nature of such experiments accidental errors of quite a few percent are to be expected. This is supported by the observation that the data of some investigators are uniformly much better than those of the others and that for more thoroughly studied explosives better agreement is obtained.

But over the accidental scattering there is superimposed a very definite trend of k which decreases with increasing density of loading. This suggests that the equation of state taken as the basis of these calculations is not exactly valid over the pressure range covered in the experiments. A better agreement might have been obtained by the use of an equation of state requiring a slightly greater dependence of covolume upon pressure. However, the available experimental detonation rate data are not accurate enough to justify a further elaboration of the theory at the present time. With the average values of k given for each

explosive one can obtain a representation of the detonation velocity curve which is within 5% of the mean of experimental data over the density range of 0.7 to 1.7 g/cc for organic explosives.

This result must undoubtedly be regarded as a considerable triumph of the theory and from the theoretical point of view it is valuable, being the first information on the behaviour of gases under conditions which might best be termed as those half-way between conditions realisable in the laboratory and those existing in the stars.

From the practical point of view, however, the theory is of little interest unless it provides the means for calculating detonation velocities for new compounds. Fortunately the theory is capable of accomplishing this task as the following will conclusively show.

In Table 5 have been collected the average values of k from Table 4, the second column giving these values corrected to 300°K with the aid of the $T^{-1/3}$ law. The third column gives the calculated values of k_{300} obtained from a set of covolumes for the individual products given in Table 6. These values have been obtained by a process of gradual fitting and could be slightly altered without impairing the excellent degree of agreement with experimental data which is shown in Table 5. Since the covolumes of CO , N_2 and O_2 were chosen as identical, there remained four arbitrary parameters to adjust for the best possible fit. The number of compounds for which excellent agreement with experimental data is obtained is greater than ten and the degree of agreement is as good as the quality of experimental data allows. Therefore the agreement is hardly an accidental one and full confidence may

be placed in calculations of k 's of new organic compounds with this set of individual covolumes unless solid carbon is formed because of oxygen deficiency. Some cases of explosive mixtures have been included in the Tables and for these an equally good agreement of theory and experiment is obtained. Thus one may safely apply the present theory to mixtures of explosives which might be developed in the search for powerful and yet safe compositions.

The individual covolumes given in the Table show a surprisingly good agreement with the van der Waals constants of these gases which have been obtained from critical data and by other methods (the critical data constants were all recomputed to 300°K using the same $T^{-1/3}$ law as for the detonation data). The detonation data seem to be somewhat higher on the average, but this in no way detracts from the success of the agreement, because extrapolation over a 15 fold range of temperature had to be made in arriving at the 300° data and a choice of only a slightly different exponent of T (for instance $T^{-1/4}$) might have eliminated the difference. For steam, however, the selected value is relatively too small; on the other hand it is well known that the law of corresponding states holds less well for steam than for other molecules here considered. The change from critical data for steam is actually in the right direction. For carbon dioxide on the other hand an excessively large covolume had to be taken while for hydrogen it is too small and we can think of no good reason why this should be so. For solid carbon 14 cc/mole was taken because at 4000°K this becomes about 6, thus giving the experimental density of graphite (2.2 at room temperature) under the conditions in the detonation wave. In the case of solid carbon (and liquid lead, see below),

the use of the expression covolume is really improper. To the extent that the gases are insoluble in the condensed phase it is the real volume of the latter per gram mole which enters into the calculations and which is given in Table 6. The assumption of the $T^{-1/3}$ temperature dependence is obviously erroneous and no physical significance should be attached to values given in Table 6 for 300°K. These are there merely for the purpose of uniformity.

The data for TNT are definitely out of line with the rest of the experimental figures whether one chooses hydrogen or water vapor as the ingredient of the detonation wave. It is to be noted however that these extreme assumptions bracket the k calculated from individual covolumes. Now, TNT is a rather cool explosive with a temperature of about 3000° in the detonation wave and at this temperature the equilibrium constant of the reaction $C + H_2O = CO + H_2$ is such (c.f. an earlier discussion) that at the high pressures of the detonation wave only partial conversion according to the above equation is to be expected. The extent of this conversion will vary of course with the density of the explosive and it is very difficult to estimate because of the non-ideality of the gas mixture. The partial conversion has little effect on the detonation velocity as was seen in Table 1, but the experimental value for k should lie between the values calculated from the individual covolume constants for the extreme cases considered. This is as found experimentally and although the treatment is not quantitative and hence cannot be regarded as particularly successful, it shows nevertheless that TNT is not in disagreement with the theory. It is, however, a good illustration of the remark made in the beginning of this report that when one of the

ingredients of the detonation wave is divided between two phases, the theory ceases to be very effective. With all other explosives tried, except possibly TNB, enough oxygen is available to oxidize all carbon to carbon monoxide and at least some hydrogen to water. The ratio $P_{CO} \cdot P_{H_2} / P_{H_2O}$ is then such that no reduction to solid carbon can take place even at 3000° or slightly below. Solid carbon found analytically among the detonation products of these explosives must be formed in the cooling process.

The treatment of lead azide leaves also something to be desired. One possible assumption is that all lead is vaporised, in which case one obtains $T_i = 3300^\circ K$ and $D_i = 1250$ m/sec. The boiling point of lead is about $1900^\circ K$ and thus at 3300° it should have a vapor pressure of only about 100 Atm., quite insignificant compared with the total pressure of the order of 10^5 Atm. This assumption is definitely erroneous therefore and our attempts to improve it by supposing that lead vapor is diatomic did not change this conclusion. One must then assume liquid lead, which gives a much higher temperature in the detonation wave (because of greater heat evolution) $T_i = 4600^\circ K$, but substantially the same detonation rate, $D_i = 1275$ because of reduced mole number of gaseous products. The calculation was carried out assuming C_{vi} for liquid lead of 6 cal per gram atom and a heat of fusion of 2 Kcal/g. atom but a reasonable change in these assumptions will not alter the D_i by more than a very few percent. The vapor pressure of lead under those conditions is undoubtedly much higher than the 100 Atm. calculated for 3300° , but in all likelihood it is still insignificant compared with the total pressure in the wave. Partial evaporation, in any case, does not seriously alter the value of D_i , since it

results in a decreasing temperature but an increasing mole number of gaseous products and these happen to compensate each other almost quantitatively in the expression for D_1 . From the experimental k one finds a volume for liquid lead of 115 cc/gr. atom at 300°K , or about 45 cc at the temperature of the detonation wave. This means a density of lead of about 4.5, a value which might appear quite unreasonable but really is not. Thus for mercury (c.f. Handbook of Chemistry, Chem. Rubber Co.) a density between 4 and 5 is reported for the critical temperature and 4600°K should be not far from the critical temperature of lead. The result of these calculations is therefore an entirely reasonable one, but of course it is very doubtful whether the theory in its present form can justifiably be applied to liquids near their critical temperatures and caution must be advised for all other explosives that may yield large amounts of liquid products in the detonation wave.

4. The search for more powerful explosives.

It seemed to us to be of some interest to establish rules that should govern the synthesis of new and more powerful explosives but unfortunately the theory is so complex that it is impossible to state such rules in a simple explicit form.

To obtain the highest possible D_1 one must have a compound with the greatest possible heat of formation (as endothermic as possible) and one that gives the greatest possible number of moles of products with the largest possible heat evolution. From the considerable amount of calculation that has been done by us it appears that the oxygen balance need not be so high as to give mainly CO_2 : the greater heat evolution in forming this compound

is compensated by the smaller number of moles formed per unit weight of the explosive and by the higher heat capacity of carbon dioxide. One of the highest D_1 thus far found is that of Cyclonite from which no carbon dioxide is formed at all. On the other hand, when the oxygen balance sinks below the amount needed to give complete oxidation to CO and H₂O, then the temperature in the detonation becomes so low that small values of D_1 are the inevitable result.

When it comes to the calculation of real detonation rates, the prediction becomes much more difficult because additional factors come into play. Steam and hydrogen have very small covolumes and therefore give small D/D_1 ratios; CO₂ on the other hand has a very large covolume and is therefore favorable. High temperatures in the detonation wave, which give large D_1 also reduce the magnitude of the covolumes and so result in smaller D/D_1 ratios. To give hard and fast rules to follow in the search for the ideal explosive under these circumstances would be presumptuous. It is suggested instead that a calculation following instructions given in Appendix II be made after the conception of a new explosive on paper and before its synthesis in the laboratory.

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Relation between D/D_1 and $k \rho_1/M$

$k \rho_1/M$	Case I ($C_V = 11.5$) Use when $\bar{\delta}_i \leq 1.22$	Case II ($C_V = 6$) Use when $1.28 \geq \bar{\delta}_i \geq 1.22$	Case III ($C_V = 6.5$) Use when $\bar{\delta}_i \geq 1.28$
0	1	1	1
0.05	1.10	1.09	1.08
0.10	1.19	1.18	1.17
0.15	1.29	1.28	1.26
0.20	1.39	1.37	1.35
0.25	1.49	1.47	1.45
0.30	1.60	1.58	1.55
0.35	1.71	1.69	1.66
0.40	1.84	1.81	1.77
0.45	1.96	1.92	1.88
0.50	2.09	2.05	2.00
0.55	2.22	2.17	2.12
0.60	2.35	2.30	2.24
0.65	2.49	2.43	2.36
0.70	2.64	2.57	2.50
0.75	2.79	2.71	2.64
0.80	2.94	2.86	2.78
0.85	3.10	3.01	2.92
0.90	3.27	3.17	3.07
0.95	3.43	3.34	3.22
1.00	3.61	3.51	3.39
1.05	3.79	3.68	3.55
1.10	3.98	3.86	3.71
1.15	4.18	4.05	3.88
1.20	4.39	4.25	4.06

Use linear interpolation between the values given.

Table 3

Variation of γ/γ_0 , of T_2/T_{21} and of a function $(x + x^2 e^x)$ with Loading Density, as Calculated on the Basis of Gas Imperfections.

$\rho, \text{k/M}$	γ/γ_0	T_2/T_{21}	$x + x^2 e^x$
0.000	1.000	1.000	0.0
0.100	0.971	0.980	0.4
0.200	0.948	0.962	0.9
0.300	0.930	0.944	1.6
0.400	0.912	0.925	2.4
0.500	0.899	0.907	3.8
0.600	0.886	0.889	5.6
0.700	0.874	0.871	7.6
0.800	0.864	0.853	10.0
0.900	0.854	0.835	12.8
1.000	0.845	0.816	16.3
1.100	0.836	0.798	20.6
1.200	0.829	0.780	26.0

Covolumes from experimental data.

Density	Detonation rate	Experimental k_T , cc	Deviation from the mean, %	Mean
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PETN. $M = 316$; $Hf_O = -123,000$ cal/mole; $T_i = 4930^{\circ}K$; $D_i = 2390$ m/sec.

Case I

Data of Friedrich				
0.50	3960	204	10	
0.65	4400	195	5	
0.80	4900	194	5	
1.00	5500	184	-1	
1.20	6300	183	-1	
1.40	7100	183	-1	
1.60	7900	181	-2	
Data of Roth				
0.45	3510	172	7	
0.75	4820	196	6	<u>185 cc at 4930°K</u>
0.91	5300	193	4	
1.04	5730	188	2	
1.45	7375	184	-1	
1.72	8050	171	-7	
Data of Tonegutti				
1.20	6070	176	-5	
1.56	7630	178	-4	
Data of others				
1.60	8200	187	1	
1.71	8340	178	-4	

Cyclonite (Hexogen); $M = 222$; $Hf_O = 21,300$; $T_i = 4650^{\circ}K$; $D_i = 2510$

Case II

Data of Tonegutti				
1.20	6310	126	2	
1.56	7890	122	-2	
Data of others				
1.67	8380	126	2	<u>124 cc at 4650°K</u>

3-Nitroglycerine; $M = 227$; $Hf_O = -82,700$; $T_i = 5230^{\circ}K$; $D_i = 2360$

Case I

Data of Friedrich				
1.59	8020	133	2	
1.73 solid,	8210	126	-4	
Data of others				
1.59	8450	141	7	
1.59	7450	123	-6	<u>131 cc at 5230°K</u>

1. Heat of formation from the elements.

Tetryl; $M = 287$; $Hf_0 = 9,300$; $T_1 = 3950^\circ$; $D_1 = 2360$

Case III

<u>Data of Friedrich</u>			
1.00	5480	181	4
1.28	6500	177	2
1.45	7210	176	2
1.54	7380	170	-2
1.61	7480	165	-5
<u>Data of Roth</u>			
0.61	2570	235 (omit)	+36%
0.92	4810	159	-8
1.24	6400	178	3
1.33	7000	185	7
1.46	7510	183	6
1.58	7665	172	0
<u>Data of others</u>			
1.53	7145	165	-4
1.59	7160	159	-8
1.65	7200	154	-11
1.68	7485	158	-8
0.96	5420	185	7

173 cc at 3950°K

Picric Acid; $M = 229$; $T_1 = 3440$; $Hf_0 = -53,500$; $D_1 = 2140$

Case III

<u>Data of Friedrich</u>			
1.03	5150	146	4
1.23	5820	135	-4
1.39	6450	135	-4
1.63	7210	131	-7
<u>Data of Roth</u>			
1.10	4560	115	-18
1.23	5430	146	3
1.34	6110	141	0
1.47	6940	149	6
1.47	6060	127	-10
1.56	7500	152	8
<u>Data of Kast</u>			
1.34	6160	142	1
1.46	6700	144	2
1.53	7000	143	1
1.60	7100	139	-2
<u>Data of Dautriche</u>			
0.90	4900	158	12
1.20	5800	147	4
1.50	7100	149	6
<u>Data of Forg</u>			
0.85	4629	153	8
1.20	5213	129	-8
1.40	6232	139	-1
1.60	7021	138	-2
<u>Data of others</u>			
0.98	4970	147	4
1.63	7600	147	4

141 cc at 3250°K

TNT; $M = 227$; $Hf_o = -13,000$; $T_i = 2950^\circ K$; $D_i = 2110$;(or $T_i = 3650^\circ$; $D_i = 2005$ if water is quantitatively formed)

Case III

<u>Data of Friedrich</u>			
1.00	4700	126	-6
1.29	5900	142	6
1.46	6500	140	5
1.57	6749	136	1
1.59	6900	138	3
<u>Data of Roth</u>			
1.21	4720	112	-16
1.27	4650	105	-22
1.40	5900	130	-3
1.52	7400	154	15
<u>Data of Kast</u>			
1.34	5940	137	2
1.45	6400	138	3
1.50	6590	138	3
1.60	6680	132	-2
<u>Data of Dautriche</u>			
0.90	4100	121	-10
1.20	5600	143	7
1.40	6600	149	11
<u>Data of Forg</u>			
0.84	4400	145	8
1.22	5396	134	0
1.45	6294	136	2
1.59	6772	135	1
<u>Data of others</u>			
1.62	7000	137	2
1.66	6365	121	-10

134 cc at 2950°K

or

141 cc at 3650°K
if H₂O is formedNitropentanone (C₉H₁₂O₁₃N₄); $M = 384$; $Hf_o = -153,000$; $T_i = 3350$; $D_i = 2230$

Case III

<u>Data of Wohler</u>			
1.13	4630	180 (omit)	-26
1.30	6020	228	-6
1.44	7170	250	1
1.59	7940	254	4

244 cc at 3350°KNitropentanol (C₉H₁₃O₁₅N₅); $M = 431$; $Hf_o = -140,000$; $T_i = 4090^\circ$; $D_i = 2400$

Case II

<u>Data of Wohler</u>			
0.75	5060	310 (omit)	26
0.91	5100	258	5
1.01	5800	279	13
1.11	5940	258	5
1.29	6100	229	-7
1.51	7050	234	-5
1.57	7360	236	-4
1.62	7540	237	-4

246 cc at 4090°K

Nitrohexanone ($C_{10}H_{14}O_2N_4$); $M = 398$; $Hf_o = -163,000$; $T_i = 2880$; $D_i = 2150$

Case III

	<u>Data of Wohler</u>			
1.18	6000	269	3	
1.25	5710	242	-8	<u>263 cc at 2880°K</u>
1.42	7000	269	2	
1.51	7740	279	6	

Nitroxenanol ($C_{10}H_{15}O_2N_5$); $M = 445$; $Hf_o = -152,000$; $T_i = 3820^{\circ}$; $D_i = 2400$

Case III

	<u>Data of Wohler</u>			
0.81	5470	335 (omit)	16	
1.00	5820	299	4	
1.28	6800	285	-1	<u>289 cc at 3820°K</u>
1.44	7670	289	0	
1.52	7900	283	-2	

TNB; $M = 213$; $Hf_o = -2,300$; $T_i = 3550$; $D_i = 2260$

Case III

	<u>Data of Dautriche</u>			
0.80	4100	112	-10	
1.10	5400	128	+3	
1.35	6700	138	+12	<u>124 cc at 3550°K</u>
	<u>Data of others</u>			
1.60	7000	122	-2	
1.63	7000	119	-4	

Mercury fulminate; $M = 284$; $Hf_o = 65,000$; $T_i = 5550^{\circ}K$; $D_i = 1640$

Case III

	<u>Data of Roth</u>			
2.21	3570	74	8	
2.70	4000	71	4	
3.27	4160	62	-8	
3.71	4810	66	-3	
	<u>Data of others</u>			
1.69	3200	80 (omit)	17	
1.81	3054	69	2	<u>67.5 cc at 5550°K</u>
1.82	3122	72	4	
2.15	3304	67	-1	
2.98	4125	67	-0	
2.99	3971	63	-7	
3.60	4500	62	-8	

Lead azide; $M = 292$; $Hf_o = -103,000$; $T_i = 4640^{\circ}$; $D_i = 1275$

Case III

	<u>Data of Roth</u>			
2.65	3850	101	7	
2.75	4420	111	19	
3.25	4700	99	6	
3.50	4830	95	2	

Lead azide (continued)

Data of Friedrich (in lead tube only; glass confinement gives utterly different results; seems probable that shock wave through glass rather than the detonation rate in the salt was measured).

2.56	4480	118	27	
3.51	4745	89	-4	
4.05	5276	88	-5	<u>93 cc at 4640°K</u>
<u>Data of Stadler</u>				
1.45	2120	70	-25	deviations from the
2.16	3080	90	-3	mean are here much
3.12	4270	93	0	greater than with other
3.19	4540	96	3	explosives investigated
<u>Data of others</u>				
3.44	4500	65	-30	

Di-PETN ($C_8H_{12}O_{18}N_6$); $M = 480$; $Hf_o = -210,000$; $T_i = 4630^\circ$; $D_i = 2340$

Case I

<u>Data of Friedrich</u>				
1.52	7000	276		<u>279 cc at 4630°K</u>
1.59	7410	282		

Glycol dinitrate; $M = 140$; $Hf_o = -56,000$; $T_i = 5300$; $D_i = 2520$

Case I

<u>Data of Naoum</u>				
1.50	8200			<u>90 cc at 5300°K</u>

C_3N_{12} , cyanuric triazide; $M = 204$; $Hf_o = 222,000$; $T_i = 4970^\circ$; $D_i = 2220$

Case III

<u>Data of Haid and Koennen</u>				
1.15	5000			<u>106 cc at 4970°K</u>

Wet Picric Acid (3.4% H_2); $M = 229$; $Hf_o = -53,500$; $T_i = 3200$; $D_i = 1970$

Case III

<u>Data of Clark</u>				
1.01	4730			<u>153 cc at 3200°K</u>

Dry Gun Cotton; (1 Kg); $Hf_o = -528,000$; $T_i = 3720$; $D_i = 2230$

Case II

<u>Data of Kast</u>				
1.30	6300			<u>368 cc at 3720°K</u>

Wet Gun Cotton; (1 Kg) $Hf_o = -1,182,000$; $T_i = 1880$; $D_i = 1640$

Case II

<u>Data of Kast</u>				
1.50	6800			<u>742 cc at 1880°K</u>

37% PETN; 10% NG; 5% DNT; (1Kg); $H_f^o = -704,000$; $T_i = 4680^{\circ}$; $D_i = 2400$
48% NH_4NO_3

Case I

1.36 Data of Naoum
6600

542 cc at 4680°K

Calculation of covolumes per mole of explosive.

Compound	T_1 °K	k_T , cc	k_{300}	k_{300} calc.	Remarks, Deviation, %
PETN	4930	185	472	459	-3
Cyclonite	4650	124	310	308	-1
Nitro-glycerine	5230	131	339	333	-2
Tetryl	3950	173	408	405	-1
Picric Acid	3440	141	318	320	+1
Wet P.A.*	3200	153	340	333	-2
TNT	2950	134	287	322	If no H_2O , only H_2 is formed
TNT	3650	141	324	303	If only H_2O , no H_2 is formed
Nitropentane	3350	244	545	543	-1
Nitropentanol	4090	246	586	604	+3
Nitrohexane	2880	263	560	573	+2
Nitrohexanol	3820	289	672	631	-6
TNB	3550	124	283	302	+7 Probably some carbon and water formed as with TNT
$Hg(OCN)_2$	5550	67.5	178	-	
PbN_6	4640	93	232		
Di-PETN	4630	279	695	705	+1
Glycol-dinitrate*	5300	90	234	230	-2
C_3N_{12} *	4970	106	270	274	+1
Dry guncotton*	3720	613	1420	1456	+2 for 1 kg.
Wet guncotton*	1880	742	1370	1410	+3 " " "
PETN- NH_4NO_3 -NG-DNT mixture*	4680	542	1360	1446	+6 for 1 kg.

* Only one experimental value available for each of these.

Covolumes of different molecules.

Substance	k_{300}, cc	van der Waals at c.p.	corrected to 300°	covolume from viscosity
N_2	38.7	38.6	30.6	39
CO	38.7	39.9	31.9	39
O_2	38.7	31.8	26.0	31 -- enters only into nitro- glycerine data
CO_2	67.0	42.6	42.5	44
H_2O	25.8	30.5	38.5	21.2
H_2	7.75	26.6	12.7	25.7
Hg	62 : chosen to fit $\text{Hg}(\text{OCN})_2$; for a close packing of spheres gives a density of about 9 instead of experimental of about 14 for solid mercury			
C (solid)	14 : chosen to give a density of about 2 at 4000°K			
Pb (liquid)	116 : gives a density of about 4.5 at 4500° ; fits PbN_6 data			

Table 7

Empirical Equations to Represent Values of
 $\int_{300}^{T_2} C_v dT = \bar{C}_v(T_2 - 300)$ in the Range 2000° T_2 5000°K .

$$\bar{C}_{v_1} = a + bT_2.$$

Substance	Equation	Accuracy
C (solid)	$\bar{C}_{v_1} = 3.94 + 0.27 \times 10^{-3} T_2$	1%
CO	$\bar{C}_{v_1} = 5.61 + 0.21 \times 10^{-3} T_2$	1%
CO ₂	$\bar{C}_{v_1} = 10.16 + 0.46 \times 10^{-3} T_2$	1%
H ₂	$\bar{C}_{v_1} = 4.91 + 0.30 \times 10^{-3} T_2$	1%
H ₂ O	$\bar{C}_{v_1} = 7.86 + 0.55 \times 10^{-3} T_2$	1%
N ₂	$\bar{C}_{v_1} = 5.54 + 0.21 \times 10^{-3} T_2$	1%

Appendix I.

Calculation of the ratio D/D_1 .

A division of equation (7) by equation (14) leads to an expression for the ratio D/D_1 :

$$\frac{D}{D_1} = \frac{v_2}{f(v_2, T_2)} \left[f'(v_2) \right]^{1/2} \left[\frac{n T_2 \sigma}{n_i T_{2i} \tau_i} \right]^{1/2} \quad (19)$$

in which all quantities may in principle be calculated from equations (8,9,10,12 and 13). This is true, of course, only if it is assumed that chemical equilibria do not shift the composition of the explosion products with density of the explosive. A discussion given in Section 3 of the report has shown that the effects of such equilibrium shifts upon the detonation velocity are very small and it has been decided therefore to neglect them altogether in this calculation. The ratio n/n_1 is assumed therefore to be unity. Actually it is somewhat different from unity (and the ratio T/T_1 is not what we calculate it below due to the same cause) but these small effects are automatically taken care of to some extent by the method of calculation, which blames all variations in D/D_1 on gas imperfections. By comparing equations (5) and (16) we note that:

$$f(v, T) = \frac{v}{1 + \frac{K}{vT^{1/3}} e^{\frac{K}{vT^{1/3}}}} \quad (20)$$

Hence, if $\frac{K}{vT^{1/3}} = x$

$$f'(v) = \frac{1 + 2xe^x + x^2e^x}{(1 + xe^x)^2} \quad (21)$$

and:

$$\frac{v}{f(v,T)} [f'(v)]^{1/2} = (1 + 2xe^x + x^2e^x)^{1/2} \quad (22)$$

If the following abbreviation is introduced:

$$C_v - \frac{R}{2xf'(v)} = \bar{C}'_v \quad \text{and} \quad C_{v_i} - \frac{R}{2x_i} = \bar{C}'_{v_i}, \quad (23)$$

and furthermore a superscript bar is used to indicate the averaging of C_v over the temperature range $T_2 - T_1$ and components of the mixture, then (c.f. equations (9), (10) and (13)) the expression for T_2 may be written thus:

$$T_2 = T_{2i} \frac{\bar{C}'_{v_i}}{\bar{C}'_v} - \frac{M}{N\bar{C}'_{v_i}} \int_{\infty}^{v_2} \left(\frac{\partial E}{\partial v} \right)_{T_2} dv \quad (24)$$

In the second term \bar{C}'_v has been replaced by \bar{C}'_{v_i} because the second term is much smaller than the first and the total variation from \bar{C}'_{v_i} to \bar{C}'_v amounts to only some 15% at the highest densities. From equation (11) the energy-volume coefficient is readily evaluated:

$$M \left(\frac{\partial E}{\partial v} \right)_T = - \frac{NRT}{3v} (xe^x + x^2e^x), \quad (25)$$

and hence:

$$M \int_{\infty}^{v_2} \left(\frac{\partial E}{\partial v} \right)_T dv = \frac{NRT_2}{3} xe^x \quad (26)$$

Therefore:

$$\frac{T_2}{T_{2i}} = \frac{\bar{C}'_{v_i}/\bar{C}'_v}{1 + \frac{R}{3\bar{C}'_{v_i}} xe^x} = \frac{1}{1 - \frac{R}{\bar{C}'_{v_i}} \left(\frac{1}{2xf'(v)} - \frac{1}{2x_i} \right) \left(1 + \frac{R}{3\bar{C}'_{v_i}} xe^x \right)} \quad (27)$$

It remains still to calculate γ . Now:

$$C_v = C_{v_i} + \frac{M}{n_i} \frac{\partial}{\partial T} \int_{\infty}^{v_2} \left(\frac{\partial E}{\partial v} \right)_{T_2} dv ; C_p = C_v + \frac{T}{n_i} \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial P}{\partial T} \right)_v \quad (28)$$

and the equation of state gives:

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{v}{T} \frac{1 + \frac{2}{3} x e^x - \frac{1}{3} x^2 e^x}{1 + 2x e^x + x^2 e^x} , \quad (29)$$

$$\left(\frac{\partial P}{\partial T} \right)_v = \frac{n_i R}{v} \left(1 + \frac{2}{3} x e^x - \frac{1}{3} x^2 e^x \right) , \quad (30)$$

$$\frac{M}{n_i} \frac{\partial}{\partial T} \int_{\infty}^{v_2} \left(\frac{\partial E}{\partial v} \right)_{T_2} dv = \frac{R}{3} \left(\frac{2}{3} x e^x - \frac{1}{3} x^2 e^x \right) . \quad (31)$$

These expressions may be substituted into the equations for C_p and C_v and thus γ obtained as a function of C_{v_i} and the variable x . This value of γ may in turn be substituted into (27) so that the temperature ratio also becomes a function only of ideal heat capacities and of the variable x .

Returning now to equation (8) and using the derived expressions for $f'(v)$ and $f(v)$ one can rewrite it thus:

$$\frac{1}{v_1} = \frac{1}{v_2} \frac{1}{1 + \frac{1 + x e^x}{\gamma (1 + 2x e^x + x^2 e^x)}} \quad (32)$$

But $1/v_1 = \rho_1/M$ and if both sides are multiplied by $\frac{K}{T_2^{1/3}}$, one obtains the relation:

$$\frac{K}{MT^{1/3}} \rho_1 = \frac{x}{1 + \frac{1 + x e^x}{\gamma (1 + 2x e^x + x^2 e^x)}} \quad (33)$$

where, of course, the complete expression for \mathcal{J}' should be substituted. Equation (33) is the same as equation (18) of the text and equation (19) above by substitution of the various quantities just obtained.

Appendix II

Computation of Numerical Values of D.

It has been explained previously that the calculation of detonation velocities is most conveniently carried out in two steps: an ideal detonation velocity is first computed for any given substance, then the actual detonation velocities for various loading densities are calculated from the ideal value with the assistance of functions previously described.

By combining equations (12) and (14) we obtain for the ideal detonation velocity:

$$D_i = \frac{\gamma_i + 1}{\gamma_i} \left(\frac{n_i R T_{2i} \gamma_i}{M} \right)^{1/2} \quad (34)$$

In this expression n_i is the number of moles of gaseous products formed by the explosion of M grams of the explosive material and γ_i is the ratio of heat capacities averaged over the gaseous products at constant pressure and constant volume and taken at the temperature, T_{2i} . The latter is to be calculated from equation (13) which will be written here in a slightly altered form.

$$T_{2i} = \frac{Hf_o - \sum n_{ji} Hf_j + T_1 \sum n_{ji} (a_j + b_j T_{2i})}{\sum n_{ji} a_j - \frac{n_i R}{2 \gamma_i} + \sum n_{ji} b_j T_{2i}} \quad (35)$$

Hf denotes heat of formation, the subscript o indicates the original explosive and the subscript j refers to one of the products of the explosion. This equation has been obtained from equation (13) by introducing the substitution:

$$-Q_o = Hf_o - \sum n_{ji} Hf_j \quad (36)$$

and the approximation

$$\int_{T_1}^{T_{2i}} c_{vj} dT = (a_j + b_j T_{2i}) (T_{2i} - T_1) \quad (37)$$

which is accurate to about 1% in the temperature range from 2000 to 5000°K. Numerical values of the coefficients a_j and b_j have been given in Table 7. The sign of H_f is taken positive if heat is absorbed in the formation of the substance. Any quantity of explosive can be made the basis of calculation provided that H_{f_0} and the various n_j 's are given values appropriate for that quantity. All H_{f_j} 's refer to one mole of the respective product. Since it is common practice to tabulate heats of formation per mole of substance, this quantity is usually the most convenient basis for calculation. Two small departures from rigor are convenient when using equation (35) for purposes of computation. The term involving T_{2i} which appears in the numerator makes an almost insignificant contribution and its value for T_{2i} equal to 4000°K can always be used without appreciable error. Likewise, in the denominator the term involving γ_i is of the order of 10% of its companion terms so that an error of 10% in the value taken for γ_i introduces only 1% error in the value for T_{2i} . Since the total range of variation of values of γ_i for substances considered in this report is only 10%, the universal use of the mean value of γ_i will introduce only 0.5% uncertainty in the value for T_{2i} . The value for $R/2\gamma_i$ is therefore taken always to be 0.80.

The calculation can, of course, be carried out for any assumed distribution of products. However, only one set of products is consistent with the theory. The rules to be followed in writing down these products have been fully discussed in the text and will

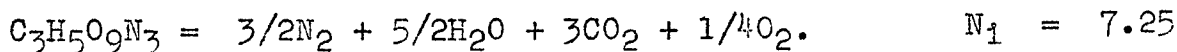
merely be repeated here. These are, 1) only solid carbon, CO, CO₂, H₂O, O₂, N₂ (and gaseous sulfur, SO₂, metals or metallic oxides, insofar as the corresponding elements are present in the explosive) are formed, and 2) oxygen reacts quantitatively to form CO, any excess then reacts quantitatively to form H₂O, and any further excess reacts quantitatively to form CO₂.

Before proceeding to illustrate the method of computation we must discuss one further convention which we have adopted in the use of equation (34). This concerns the quantity \bar{h}_i which should be taken at the temperature calculated from equation (35). In order to obtain the value, as defined, a further procedure is required which involves the use of tables of heat capacities at various temperatures from which appropriate values are to be found for each of the product substances, after which a summation must be carried out over all of the products. This procedure is fairly tedious. However, an approximation which results in values of D_i that are uniformly about 2% too low, but which eventually leads to values of D for actual conditions from which this error has been eliminated is very simple. Call the denominator of equation (35) d . Then it can easily be shown that

$$\frac{\bar{h}_i}{h_i} = \frac{d + 2.8 n_i}{d + 0.8 n_i} \quad (38)$$

As stated, the use of this approximation in equation (34) results in values of D_i which are 2% low, but since we have used this procedure consistently for all calculations the error is compensated by our choice of covolumes required for the second stage of the calculation and given in Table 6.

A sample calculation is now given for the example of Nitroglycerin. The calculation is based on one mole, 227 grams, for which the proper decomposition equation is:



$$\text{Hf}_0 = -82,700 \text{ cal./mole}, \text{Hf}(\text{H}_2\text{O}_{\text{gas}}) = -57,870, \text{Hf}(\text{CO}_2) = -94,240.$$

n_j	$n_j \text{Hf}_j$	$n_j a_j^{1)}$	$n_j b_j^{1)}$
$\text{N}_2 = 3/2$		8.31	0.32×10^{-3}
$\text{H}_2\text{O} = 5/2$	-144,675	19.65	1.37×10^{-3}
$\text{CO}_2 = 3$	-282,720	30.48	1.38×10^{-3}
$\text{O}_2 = 1/4$		1.42	0.05×10^{-3} (estimate)

$$\begin{array}{r}
 - N_j \text{Hf}_j = 427,395 \quad N_j a_j = 59.86 \quad N_j b_j = 3.12 \times 10^{-3} \\
 + \text{Hf}_0 = -82,700 \\
 \hline
 344,700
 \end{array}$$

$$T_{2i} = \frac{344,700 + 300 (59.86 + 3.12 \times 10^{-3} \times 4 \times 10^3)}{59.86 - 7.25 \times 0.80 + 3.12 \times 10^{-3} T_{2i}}$$

$$T_{2i} = \frac{366,400}{53.80 + 3.12 \times 10^{-3} T_{2i}}$$

$$\text{Assume } T_{2i} = 5 \times 10^3; \text{ Calculate } T_{2i} = \frac{366,400}{53.80 + 15.60} = \frac{366,400}{69.40} = 5280^\circ \text{K}$$

$$\text{Assume } T_{2i} = 5.20 \times 10^3; \text{ Calculate } T_{2i} = \frac{366,400}{53.80 + 16.20} = \frac{366,400}{70.00} =$$

5230°K (accept.)

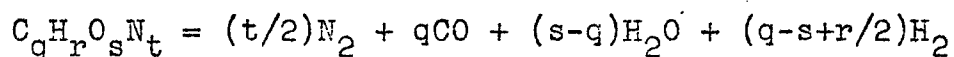
$$d = 70.00; \quad = \frac{70.00 + 2.8 \times 7.25}{70.00 + 0.8 \times 7.25} = \frac{89.6}{75.1} = 1.20$$

$$D_i = \frac{2.20}{1.20} \frac{7.25 \times 5.23 \times 8.31 \times 1.20^{1/2}}{227} \times 10^3 \text{ m/sec.} = 2360 \text{ m/sec.}$$

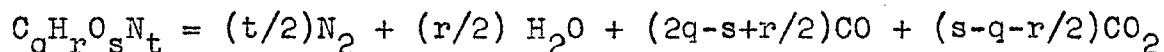
With the exception of nitroglycerin, T.N.T. and the salts of metals, the calculations for all other substances mentioned in this report can be still further simplified as follows: If the formula of the substance be written as $C_qH_rO_sN_t$, then $q \leq s \leq 2q + r/2$; that is, there is at least enough oxygen to convert all carbon to CO but no more than necessary to oxidize all hydrogen and carbon to H_2O and CO_2 respectively. It seems almost certain that the majority of the compounds likely to be formed from these four elements in the search for new and powerful explosives will answer the above description. During the course of this investigation, it was found convenient to convert equation (35) into general expressions involving q, r, s and t . These are somewhat simpler to use and furthermore require less exercise of judgment, or rather, attention to rules, and do away with the necessity for reference to several of the tables. In the interest of convenience, their use is strongly recommended whenever possible.

When $q \leq s \leq 2q + r/2$ for a substance of composition $C_qH_rO_sN_t$ it will decompose according to one or the other of two equations.

A. If $q + r/2 \geq s$, then we write:



B. If $q + r/2 \leq s$, then we write:



Introducing the expressions for the n_j 's in terms of q, r, s and t along with the appropriate numerical quantities taken from Table 7 and the numerical values for the heats of formation of CO, CO_2 and H_2O ; then proceeding exactly as outlined before in this appendix and as illustrated for nitroglycerin one obtains the two equations:

$$q + r/2 \geq s \quad Hf_0 - 29,843q + 1,222r + 58,368s + 948t \quad (39)$$

$$T_{2i} = \frac{(1.86q + 2.06r + 2.95s + 2.37t) + (-0.04q + 0.15r + 0.25s + 0.11t) \cdot 10^{-3} T_2}{1}$$

$$q + r/2 \leq s \quad Hf_0 - 40,724q - 4,218r + 69,249s + 948t \quad (40)$$

$$T_{2i} = \frac{(0.26q + 1.26r + 4.55s + 2.37t) + (-0.04q + 0.15r + 0.25s + 0.11t) \cdot 10^{-3} T_2}{1}$$

For both cases the equivalent of equation (34) becomes:

$$D_i = \frac{\delta_i + 1}{\delta_i} \left(\frac{t/2 + r/2 + q}{12q + r + 16s + 14t} \cdot 8.31 \delta_i^{1/2} T_{2i} \cdot 10^{-3} \right)^{1/2} 10^3 \text{ m/sec.} \quad (41)$$

The use of one of these equations is illustrated by the following example, a calculation for cyclonite.

To systematize the calculation it is convenient to consider both equations (39) and (40) to be of the form

$$T_{2i} = \frac{Hf_0 + \sum f_i x_i}{\sum g_i x_i + 10^{-3} T_2 \sum h_i x_i} ; x_i = q, r, s, t. \quad (42)$$

Calculation for cyclonite, $C_3H_6O_6N_6$. $q + r/2 = 3 = s = 3$.

Can use either (39) or (40). Arbitrarily choose (40).

x_i	$f_i x_i$	$g_i x_i$	$h_i x_i$
$q = 3$	-122,172	0.78	-0.12
$r = 6$	- 25,308	7.56	0.90
$s = 6$	+415,494	27.30	1.50
$t = 6$	5,688	14.22	0.66
	<u>+421,182</u>	sum=49.86	3.06
	<u>-147,480</u>		<u>-0.12</u>
	sum = 273,700		sum = 2.94
	+ $Hf_0 =$ <u>21,300</u>		
	<u>295,000</u>		

$$T_{2i} = \frac{295,000}{49.86 + 2.94 \times 10^{-3} T_2}$$

$$\text{Assume } T_{2i} = 4.5 \times 10^3; \text{ Calculate } T_{2i} = \frac{295,000}{49.86 + 13.21} = \frac{295,000}{63.07} = 4680^\circ \text{K}$$

$$\text{Assume } T_{2i} = 4.65 \times 10^3; \text{ Calculate } T_{2i} = \frac{295,000}{49.86 + 13.68} = \frac{295,000}{63.54} = 4650^\circ \text{K accept.}$$

$$\bar{y}_i = \frac{63.54 + 2.8 \times 9}{63.54 + 0.8 \times 9} = 1.28$$

$$D_i = \frac{2.28}{1.28} \left(\frac{9 \times 8.31 \times 4.65 \times 1.28}{222} \right)^{\frac{1}{2}} = 2510 \text{ m/sec.}$$

When the value of D_i has been obtained for a given substance it becomes a relatively simple matter to predict the detonation velocity for various loading densities. According to the theory given in the text, D/D_i is a function of $k \rho_i / M$ where D is the detonation velocity at the loading density, ρ_i , and k is the covolume of the products resulting from decomposition of M grams of the explosive at the temperature of the explosion. We begin by calculating a value of k at 300° . The sum is taken (over all products), of the number of moles of each product multiplied by its covolume as given in Table 6. This sum is then multiplied by $(300/T_{2i})^{1/3}$ to obtain the covolume at the temperature of the explosion. Further multiplication by the desired loading density and division by M then gives the quantity which is related to D/D_i . Numerical values of D/D_i as a function of numerical values of $k \rho_i / M$ are given in Table 2 for three different values of \bar{y}_i as defined in equation (38).

To illustrate we consider cyclonite which decomposes by the equation: $\text{C}_3\text{H}_6\text{O}_6\text{N}_6 = 3\text{N}_2 + 3\text{CO} + 3\text{H}_2\text{O}$ $T_{2i} = 4650^\circ \text{K}$ and $D_i = 2510 \text{ m./sec.}$ From Table 6 we find $k_{3000} = 3(38.7) + 3(38.7) + 3(25.8) = 308$. Then $k_{46500} = 308(300/4650)^{1/3}$ and for $M = 222$ and $\rho_i = 1.20$ we obtain $k \rho_i / M$ at $4650^\circ \text{K} = 0.665$. Observing that

\bar{f}_i for cyclonite is 1.26 and consulting Table 2 we find in the 3rd column that the corresponding value of D/D_1 is 2.47. Hence we predict $D = 2.47 \times 2510 = 6180$ m/sec at $\rho_1 = 1.20$ g/cc. If it is desired to calculate the real temperature in the detonation wave, the knowledge of T_1 and column 3 of Table 3 make this very simple. To obtain the real pressure in the detonation wave one may use an equation which follows from the theory developed in this report:

$$P_2 = \frac{nRT_2}{K} (x + x^2 e^x) \quad (43)$$

After calculating k as discussed previously, one may take the values of the function $(x + x^2 e^x)$ from the last column of Table 3 and thus obtain P by equation (43) in which $R = 82$ cc. Atm.

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Z. S. S. = Z. für das gesamte Schiess - and
Sprengstoffwesen.