DEPENDENCE OF DAMAGE EFFECTS UPON DETONATION PARAMETERS OF ORGANIC HIGH EXPLOSIVES[1]

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CONTENTS

I. INTRODUCTION

A high explosive is a material capable of an energy release of the order of magnitude of 1000 cal./g. and of a very rapid rate of release of that energy. A high explosive is sometimes called a secondary explosive because it is also capable of a comparatively slow release of energy; it can burn without detonating. An organic high explosive is composed of carbon, hydrogen, nitrogen, and oxygen atoms; most of its useful oxygen is weakly attached through nitrogen as in the nitro, nitramino, and nitrate groups. By definition, the organic high explosive is capable of undergoing an extremely rapid, exothermic decomposition to stable products. The organic high explosive is, therefore, thermodynamically unstable with respect to its decomposition products (large negative change in free energy), but also exhibits a fairly large activation energy (30–40 kcal./mole). Thus it is harder to initiate the decomposition of an organic high explosive than that of many nonexplosive organic compounds. Once the decomposition of the explosive has been started, however, the reaction is self-propagating.

High explosives can react in a variety of ways, including the extremes of smooth burning and of steady-state detonation. In burning, ordinary physicochemical mechanisms are involved, and propagation is effected by transport

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[1] This work has been reported in greater detail in Naval Ordnance Laboratory Reports 4230, 4510, 5678, and 6238. The material contained in this paper was declassified by the Naval Ordnance Laboratory on December 29, 1958, and has been presented, in part, before the Division of Industrial and Engineering Chemistry at the 135th Meeting of the American Chemical Society, Boston, Massachusetts, April, 1959.

phenomena. This results in a relatively low velocity of flame propagation, but can nevertheless cause damage, especially if the reaction occurs in a closed space. This behavior is frequently termed "explosion." Detonation, on the other hand, is chiefly a hydrodynamic phenomenon and is propagated by shock waves travelling at supersonic velocities. When conditions are such that a maximum steady-state velocity (about 7000 m./sec. for a solid explosive) of the reaction front is achieved, detonation reactions follow a well-known thermohydrodynamic theory which has been summarized elsewhere (12, 37). During detonation, the explosive decomposes very rapidly to its stable products, chiefly gases, which are, at the moment of formation, denser than the original explosive. Detonation is consequently characterized by very high pressures as well as by high and rapid release of energy.

The damaging ability of an explosive has frequently been considered in terms of its brisance (breaking and shattering ability) and its power (total work capacity) (10). These are not well-defined terms, but their qualitative meaning can be described. Target damage must result from the force exerted upon the target, the time profile of that force, and the strength properties of the target. Hence the pressure–time history experienced by the target as a result of the detonation, combined with the structural characteristics of the target, determine the nature and extent of the damage. Qualitatively, brisance corresponds to the portion of the pressure–time curve above the yield point of the target, while power reflects the entire curve. In this review, the less exact terms of brisance and power are replaced by the well-defined parameters of detonation pressure and detonation energy, respectively. These parameters are not only exact, but they are defined by the explosive itself and not, in part, by the properties of the target. It is obvious from detonation theory that these parameters cannot be varied independently; nevertheless it can be shown that some effects, notably those on a primary metal target adjacent to the explosive, depend chiefly on the pressure, while others show greater dependence on the energy.

All explosive effects must ultimately be determined by the basic physical and chemical properties of the explosive. Similarly, all explosive effects must be related to one another. Because the dependence of effects and properties is complicated, very few clear-cut relationships have been demonstrated. Some years ago, Lothrop and Handrick (20) used small-scale test data accumulated in many laboratories to indicate the effect of the constitution of an explosive on its performance. While Schmidt (31) justifiably criticized certain details of their treatment, their view that such relationships should exist seems sound.

The severe limitations of small-scale laboratory tests as estimates of explosive performance are now generally recognized (10). In particular, the Trauzl lead block and the ballistic pendulum tests of earlier work (20) are now both considered but qualitative measures of power (10) rather than of brisance and power, respectively. In the last ten years, a sufficient amount of precisely measured damage data have become available to make recourse to the small-scale tests unnecessary.

The present study is concentrated on field-scale damage tests as a measure of explosive performance. Moreover, it includes a sufficient variety of explosives to furnish a large range in the numerical values associated with each measured effect. To assure that the data were obtained under known and controlled test conditions, and were internally consistent, the study has been confined, with a few exceptions, to measurements made in this laboratory.

For these data it has been possible to show that the fragment velocity, shaped-charge penetration, airblast, and underwater effects are related to the explosive properties of detonation energy and pressure. A representative sample of the data will be presented to illustrate each of the empirical relationships found.

It was found that the explosive characteristics most useful for a correlation of the effects were the detonation parameters: energy, pressure, and velocity. Of these, the detonation velocity can be measured directly (4), the pressure can be measured indirectly (8, 11), and the energy can probably be measured directly (28, 36). Unfortunately, measurements of the pressure have been reported for only four organic explosives and measurements of the energy for only six.

It is important to know not only the relationships which exist but also those which for theoretical reasons cannot exist. Since detonation velocity can be measured simply and precisely, there is a temptation to attempt to predict explosive performance from rate data alone. Because oxygen balance can be exactly defined and computed, it is frequently misused for prediction. The structural formula of an explosive molecule will give some information about certain properties of the explosive, but it too is limited in its usefulness for prediction. Examples of fortuitous invalid relationships involving these three quantities are frequent. Consequently an effort has been made in this review to indicate the limitations as well as the usefulness of each of them.

II. EQUATION OF STATE AND DETONATION PARAMETERS

The energy released in the detonation front depends on the products of the chemical decomposition of the organic explosive. The nature of these products and their concentrations can, in principle, be calculated by using a specific equation of state for the products and making an equilibrium computation for the detonation temperature and pressure indicated by the equation of state used in conjunction with the well-known hydrodynamic equations of detonation theory (7, 12, 37). While the detonation pressure and velocity are relatively insensitive to the equation of state chosen for the products (7, 18), the equilibrium composition of the products and consequently the energy released and the detonation temperature are extremely sensitive to this choice. Machine computations are now being used in studies designed to select a realistic equation of state (13). The results now available demonstrate the extreme complexity of the problem and indicate that its solution will require a great deal of additional work.

Since the theory is not sufficiently advanced to indicate the true equation of state, a simple one which has been used with surprising success in applications to detonation problems was selected. This is the equation for the polytropic gas:

$$P = A\rho^K \tag{1}$$

where P is pressure, ρ is density, and A and K are constants. Various workers (16, 17, 25) have derived the detonation relations reuslting from the use of equation 1 and have applied them for the case of $K = 3$. In particular, Jones and Miller (17) showed that most of the energy of the gases was released very early in the adiabatic expansion, and Jacobs (16) reproduced the detonation pressures computed by use of a much more elaborate equation of state (7) for cyclotol 65/35. Recently, Deal (9) made an experimental measurement of the pressure–density values of the detonation products of a very similar explosive. He found that the P vs. ρ behavior was well reproduced by equation 1 with a K value of 2.77.

In the present work, the most useful equations resulting from combining equation 1 with the hydrodynamic equations of detonation theory are

$$P = \frac{\rho_0 D^2}{K + 1} \tag{2}$$

and

$$Q = \frac{D^2}{2(K^2 - 1)} \tag{3}$$

where P = detonation pressure,
D = detonation velocity,
Q = detonation energy, and
ρ_0 = loading density of explosive.

The usual approximation of neglecting the initial ambient pressure as compared to the detonation pressure is made. The three detonation parameters are quantitatively related by equations 2 and 3. If the velocity and pressure are measured, the adiabatic exponent and therefore the energy can be computed. Alternatively, if the velocity and energy are measured, the adiabatic exponent and the pressure can be computed. Because neither pressure data nor energy data are generally available, an independent method of approximating one of these parameters is necessary to supplement the measured detonation velocity in computing the second parameter. It was decided to estimate the detonation energy in order to compute the detonation pressure.

An estimate of the energy or heat of detonation was obtained by using an arbitrary decompositon mechanism which assigns the oxygen in the explosive to the formation of water vapor, carbon monoxide, and carbon dioxide in that order. The resultant heat of reaction at 25°C. and 1 atm. is computed from the heats of formation of the products and of the explosive. This mechanism was chosen because the energies computed by it agree fairly well with calorimetrically determined heats of detonation. (For pure organic explosives such determinations may equal the actual energy released in the detonation front. Because of the possibility that the detonation products are not cooled rapidly enough to freeze the mixture at its detonation composition, there remains some doubt.) The only available calorimetric determinations are those of the British.[2]

[2] After the present work was completed, Apin and Lebedev (1) published data on the heat of detonation for RDX. Their results were higher than those reported by the British; indeed, at a density of 1.78 g./cc., the value reported was 1420 cal./g. To compute this large a value, it is necessary to assume that all of the carbon has been converted to carbon dioxide and that 60 per cent of the hydrogen has been converted to ammonia.

TABLE 1

Comparison of computed with calorimetric heats of detonation

Explosive	Heat of Detonation	
	Computed from arbitrary mechanism	Calorimetric (2)*
	cal./g.	*cal./g.*
PETN	1416	1450
RDX	1228	1324
Cyclotol 50/50	1106	1158
Tetryl	1047	1107
Picric acid	784	1032
TNT	984	1013

* Reference.

TABLE 2

Comparison of derived and computed energies of detonation

Explosive	Loading Density ρ_0	Measured Values from Reference 7		Derived Values		Detonation Energy (Computed from Arbitrary Mechanism)
		Detonation velocity D	Detonation pressure	Adiabatic exponent K	Detonation energy Q	
	g./cc.	*m./sec.*	*kbar.*		*cal./g.*	*cal./g.*
RDX	1.800	8754	341	3.06	1107	1228
Cyclotol 78/22	1.755	8306	317	2.82	1187	1174
Cyclotol 65/35	1.715	8036	292	2.79	1135	1143
TNT	1.640	6950	177	3.48	521	984

Robertson and Garner (28) first developed a special calorimeter required to contain a detonation. Sutton's work (36) with it clearly showed the effect of confinement and loading density on the measured heat of reaction, and hence the need of a large-scale determination if the maximum possible energy release is to be realized. (The effects data were obtained on dense charges, i.e., for loading densities at about 90–100 per cent crystal density.) Comparisons of the computed and calorimetric values are shown in table 1.

The arbitrary decomposition mechanism chosen underestimates the calorimetric heat of detonation by less than 8 per cent except for picric acid; a similar discrepancy for this explosive was observed in correlating the data for underwater effects. In addition, the arbitrary mechanism yields a good approximation to the detonation energies derived from measured velocities and pressures. Table 2 shows this comparison for the few explosives on which precise measurements of both velocity and pressure have been reported. The agreement is good except for TNT. The much more elaborate treatment of Cowan and Fickett (7) also resulted in a large and unexplained discrepancy between the experimental and computed values of the adiabatic exponent for this explosive; their theoretically computed K value gives a detonation energy in better agreement with both the calorimetrically measured value and the approximate value obtained with the arbitrary mechanism. The discrepancy may arise from an inadequate equation of state for the products of high carbon content or from inadequate information about the formation of the solid carbon, but as the subsequent relations show, use of an "effective" adiabatic exponent derived from the measured detonation velocity and estimated detonation energy seems adequate for the present work.

The ability of an arbitrary mechanism to produce a good estimate for the heat of a reaction without necessarily representing the true reaction products can only result from a number of compensating factors. The obvious ones in the present case are (*1*) that the water gas equilibrium has little effect on the heat of reaction, since the heat of formation of the products differs from that of the reactants by only about 10 per cent, and (*2*) the high detonation pressures shift the soot reactions to favor greater energy release. The soot reactions are

$$2CO \rightleftharpoons CO_2 + C$$

$$H_2 + CO \rightleftharpoons H_2O(g) + C$$

and both are shifted to the right as the pressure increases. This is shown by equilibrium computations; the variation of the detonation products with the loading density of cyclotol 65/35 (7) is a good illustration.

III. EFFECTS OF EXPLOSIVE STRUCTURE

A. General considerations

The structure of an organic molecule, i.e., the active chemical groups and how they are bound together, would be expected to influence only three quantities of any importance to the explosive behavior. These are the kinetics of its decomposition, its heat of formation, and the fuel-to-oxygen ratio of its atomic constituents.

Inasmuch as the structural formula tells what chemical bonds are present, it provides information to be supplemented by a knowledge of bond strengths which leads, in principle, to a knowledge of the weakest bond and the amount of energy necessary to break it. Thus, in principle, the structure gives some information about the minimum energy necessary to start the decomposition of the molecule. This is the energy of activation which controls, in part, the kinetics of decomposition. A minimum rate of decomposition is a necessary though not a sufficient condition for a high explosive. In this sense, the structure determines whether a material is an explosive. Practically no quantitative work has been done on the chemical kinetics of detonation phenomena.

The most obvious structural effect is upon the heat of formation of the explosive itself. Group contributions to the standard heat and free energy of formation are well established (5, 19). For example, introduction of a hydroxyl group will increase the molecular heat of formation by about 50 kcal., while a nitro group will raise the value by about 20. If the latent heat of fusion of the solid explosive is known or assumed, its heat of formation can easily be computed from its structure.

The heat of formation does have some effect, though in the case of organic explosives a minor one, on the heat of reaction. If the general reaction is

$$A \rightarrow \Sigma \nu_i B_i$$

then the heat of reaction at 1 atm. and 25°C. is

$$Q_{\text{reaction}} = \Sigma \nu_i Q_i - Q_e \tag{4}$$

where Q_i = standard heat of formation of product i
= $-\Delta H^\circ_{fi}$ (298°K.), and is positive if the formation of the compound from its elements in the standard state is an exothermal process, and
Q_e = standard heat of formation of the explosive.

For organic explosives, the last term of equation 4 is small (less than 10 per cent of the total). Hence the variation in the energy released can be small for a large structural change.

Although the contribution of the heat of formation to the heat of reaction is relatively small, it is not completely submerged if the data are sufficiently accurate. Inadequacy of a computed approximate heat of formation value (subsequently corrected by an experimental determination) was first detected for several explosives by their marked departure from the underwater effects–energy relationship described in Section IX.

The major contribution to the heat of reaction, $\Sigma \nu_i Q_i$, is determined by the nature and amount of the various products. For organic explosives the chief products are:

B_i	Q_i (29)	B_i	Q_i (29)
	kcal./mole		*kcal./mole*
H_2O(g)	57.798	C	0
CO	26.416	N_2	0
CO_2	94.052	H_2	0

The composition of the products will depend largely on the relative numbers of carbon, hydrogen, nitrogen, and oxygen atoms within the molecule. In other words, it will depend on the total amount of fuel, the fuel-to-oxygen ratio, and the various types of fuels involved. One gram-atom of oxygen can be used as follows:

	Energy released
	kcal.
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g)$	57.8
$C + \frac{1}{2}O_2 \rightarrow CO$	26.4
$\frac{1}{2}C + \frac{1}{2}O_2 \rightarrow \frac{1}{2}CO_2$	47.0
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	67.6

Inasmuch as introduction of different chemical groups into the molecule will change the fuel–oxygen ratio and shift the importance of the various possible oxidation reactions, the structure does have a part in determining $\Sigma \nu_i Q_i$. It is not, however, a very direct relationship, and the molecular formula gives as much information about it as does the structural formula.

B. Oxygen balance

There is no complex quantitative index which includes all the important factors: the total fuel, the fuel–oxygen ratio, and the relative role of the possible oxidations. The last would require equilibrium computations for which adequate information is still unavailable. There is, however, an index used for one of these factors, the fuel–oxygen ratio. This is the oxygen balance, which is frequently used and occasionally misused.

If the generalized molecular formula of the explosive is

$$C_aH_bN_cO_d \tag{5}$$

then the oxygen balance to the carbon dioxide level is

$$\text{O.B. to } CO_2\,(\%) = \frac{d - 2a - 0.5b}{\text{molecular weight}}\,1600 \tag{6}$$

The oxygen balance of equation 6 is an exact expression of the amount of additional oxygen, over the molecular content d, which must be supplied to burn all of the hydrogen and carbon in the molecule $C_aH_bN_cO_d$ to water and carbon dioxide. By definition

$$-\frac{\text{O.B.}}{100} = \Delta O_c \tag{7}$$

where ΔO_c is the additional oxygen in grams per gram of explosive needed for complete combustion. Since oxygen balance tells nothing about the absolute amount of fuel (or oxygen) already present in the molecule, it cannot be expected to give any information about the heat of decomposition, i.e., detonation energy. On the other hand, it might yield information about energy available from combustion of the decomposition products if the fuel composition of the products is known.

Two simple illustrations help to clarify these statements. Suppose Mr. X is in process of buying a house, and it is known that he has already paid a deposit which is \$4000 less than the cost of the house. His "dollar balance" is then −\$4000, and the information available is:

$$\text{Deposit} - \text{dollar balance} = \text{cost of house}$$

Note that the dollar balance tells nothing of the size of either the deposit or the cost. The comparable information about the explosive is

$$\text{Oxygen present} - \frac{\text{O.B.}}{100} = \text{total oxygen needed for complete combustion of constituent H and C}$$

or

$$\Delta O_c = O_c - \text{oxygen present}$$

The analogy can be carried no further, because each dollar has the same purchasing power, whereas the purchasing power of the oxygen depends upon the fuel with which it combines.

When it is possible to interpret the amount of oxygen in terms of heat produced by its reaction, the total oxygen for combustion, O_c, would be related to the heat of combustion:[3]

$$Q_c\ (\text{cal./g.}) = \frac{94050a + 57800 \times \frac{1}{2}b - Q_e}{\text{molecular weight}}$$

The oxygen present in the molecule would be related to the heat of detonation Q. Thus ΔO_c would be related to $(Q_c - Q)$, and to show how this quantity can vary, a reaction mechanism must be assumed. For the arbitrary decomposition already described, the decomposition reaction, applied to explosives of $b \leq 2d$, would be

$$C_aH_bN_cO_d \rightarrow \begin{cases} \frac{1}{2}bH_2O + (d - \frac{1}{2}b)CO + \frac{1}{2}cN_2 + (a - d + \frac{1}{2}b)C & 0 \leq (d - \frac{1}{2}b) \leq a \\ \frac{1}{2}bH_2O + (d - \frac{1}{2}b - a)CO_2 + (2a - d + \frac{1}{2}b)CO + \frac{1}{2}cN_2 & a < (d - \frac{1}{2}b) \leq 2a \\ \frac{1}{2}bH_2O + aCO_2 + \frac{1}{2}cN_2 + \frac{1}{2}(d - \frac{1}{2}b - 2a)O_2 & (d - \frac{1}{2}b) > 2a \end{cases}$$

Consequently

$$(Q_c - Q) = \begin{cases} \dfrac{a}{\text{M.W.}} 41220 + 16.51\Delta O_c & \text{Below level for } H_2O \text{ and } CO \\ 42.90\Delta O_c & \text{Between } CO \text{ and } CO_2 \text{ levels} \\ 0 & \text{Above } CO_2 \text{ level} \end{cases} \qquad \underline{\text{Oxygen balance}}$$

So while a single value of the oxygen balance corresponds by definition to a single value of ΔO_c, it is entirely possible to have several different explosives with the same value of ΔO_c correspond to several different values of $(Q_c - Q)$. This happens in the mechanism illustrated for explosives of oxygen content too low to convert all the carbon and hydrogen to water and carbon monoxide, i.e., where the available fuel consists of both carbon and carbon monoxide. The additional heat available through use of the extra oxygen supplied after the detonation is not defined in this region without a knowledge of the number of carbon atoms per gram of explosive as well as the oxygen balance. In the region between the carbon monoxide and carbon dioxide levels, however, $(Q_c - Q)$ is uniquely defined by the oxygen balance because only one fuel (carbon monoxide) is involved.

While the mechanism used for illustrative purposes is arbitrary, its use does not invalidate the general conclusions. Oxygen balance is an excellent measure of the additional oxygen required for complete combustion; it can furnish no information about the heat of detonation, but in certain restricted and unknown

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[3] For simplicity in this example, the value of the heat of formation for water as vapor rather than liquid is used.

regions it can give information about the additional energy that can be obtained by burning the detonation products.

Another oxygen balance which has been defined and used is

$$\text{O.B. to CO }(\%) = \frac{d - a - \frac{1}{2}b}{\text{molecular weight}}\,1600$$

$$= \text{O.B. to CO}_2 + \frac{a}{\text{molecular weight}}\,1600 \tag{8}$$

This balance is related to that of equation 6 in an indirect way again, because several fuels are involved.

IV. DETONATION VELOCITY

It is evident that measured values of the detonation velocity must be used in any applications of equations 2 and 3. Although the detonation velocity D can, indeed, be measured more precisely than many other explosive phenomena, the available data are by no means as precise as could be desired. Moreover, the value of D in equations 2 and 3 is the ideal or infinite-diameter value (12), whereas the measured values are affected not only by the finite charge diameter, but also by the uniformity of the charge, and, in the case of optical measurements, by camera calibration and by distortion of the wave front at the charge surface. Determinations made at this laboratory are generally on cylindrical charges 1⅝ in. in diameter and 12–15 in. long by use of a rotating-mirror camera (3). The precision for an average of three shots is ±100 m./sec. in D and ±1 per cent in the loading density ρ_0. When several determinations have been made at different loading densities to define a linear region of the D vs. ρ_0 curve, and the curve is then used to obtain detonation velocities at intermediate densities, the overall precision may be only ±3 per cent. If, as is sometimes the case, no study of the diameter effect has been made, the experimental value may differ from the ideal by ±5 per cent. This is still good precision for an experimental measurement on explosives. Nevertheless, it should be noted that the detonation velocity occurs as a square in the theoretical relations. Hence an error of 5 per cent in D will increase the error in computing other detonation parameters to about 10 per cent. Thus an error in the detonation velocity accompanied by a comparable error in a second parameter may make an exact relationship seem very qualitative indeed.

The tables which follow list the detonation velocity values used in the present work. For pressed TNT, RDX, and cyclotols these are values obtained on very carefully prepared, large charges at Los Alamos (7). Measurements were made there by the pin technique (4), which is capable of a velocity precision of ±10 m./sec.; the error involved in using the derived D vs. ρ_0 curve is presumably larger but certainly less than in the work at this laboratory. Detonation velocities for other materials are, unless otherwise indicated, values determined at this laboratory.

A recent publication (22) has attempted to demonstrate that the detonation velocity of an organic high explosive is a simple function of its loading density and its modified oxygen balance. It was argued that an oxygen balance similar to that of equation 6 (the quantity defined was on a per atom rather than a per gram basis) should be corrected by weighting each oxygen atom present according to its accessibility, i.e., according to the strength of the bond attaching it to the molecule. Thus the oxygens in N=O, C—O—N, C—O—H, and C=O were assigned the respective weights of 0, 1, 2.2, and 1.8. The last two weights were assigned in the proportion of the corresponding group contributions to the energy of formation of the molecule. The correction term was assigned the same sign as the uncorrected oxygen balance. (This assignment does not define the correction for a zero oxygen balance. Moreover, the basis for making the correction in the first place seems to require that it always be subtracted.) The corrected oxygen balance Ω was then considered to be a unique measure of the potential energy (detonation energy) of the explosive molecule. It was then assumed that the detonation velocity should be a simple linear function of the detonation energy through Ω, and that the change of detonation velocity with loading density, $\mathrm{d}D/\mathrm{d}\rho_0$, would also be a linear function of detonation energy through Ω. Examination of the available data then led to the relations

$$D = \alpha + \beta\Omega \ (\pm 2\% D) \quad \text{for} \quad \rho = 1.6 \text{ g./cc.} \tag{9}$$

$$\frac{\mathrm{d}D}{\mathrm{d}\rho_0} = \gamma + \delta\Omega\left(\pm 5\% \frac{\mathrm{d}D}{\mathrm{d}\rho_0}\right) \tag{10}$$

where α, β, γ, and δ are constants.

The derived general relationship of D as a simple function of ρ_0 and Ω was said to reproduce the experimental values of the detonation velocity within 2 per cent without the assumption or use of either a decomposition mechanism or an equation of state for the detonation products.

It has already been shown in Section III that the oxygen balance cannot give information about the detonation energy. Modification of the oxygen balance according to availability of the oxygen does not improve the possibility of obtaining such information. On the other hand, the modified oxygen balance may be closely related to the ease of *initiating* detonation or the explosive sensitivity. Explosive mixtures such as those of hydrogen and oxygen are notoriously more sensitive as the stoichiometric composition is approached. Ease of initiation is associated with the thermodynamic functions of activation and hence with the chemical kinetics of decomposition. The kinetics are unrelated to the energy released by the decomposition and, indeed, beyond a minimum rate requirement, the detonation velocity is independent of the rate of chemical decomposition (12, 26).

For the simple theoretical treatment and equation 3 of Section II,

$$D^2 = 2Q(K^2 - 1)$$

If the adiabatic exponent K were the same for each explosive, the detonation velocity D would be a parabolic function of the energy; at large values of D, there might even be sections of the parabola well approximated by a straight line. However, K does not remain constant; the few experimentally derived values show a variation of 2.79 to 3.48 (7). It follows that a linear relationship between the detonation velocity and energy is theoretically unsound.

The apparent success of equation 9 arises from examination of a restricted group of explosives, all of which are quite similar. A variance arrangement of equation 9 shows that for detonation velocities of 6800–8400 m./sec., the range at $\rho_0 = 1.60$ g./cc. for the group of explosives treated, Ω may vary from 8 to 100 per cent and still cause only 2 per cent variation in detonation velocity.[4] It is easy to find exceptions to equation 9. For example, both trinitroethyl trinitrobutyrate (TNETB) and cyclotrimethylenetrinitrosoamine (24) show marked departure from its predictions.

Equation 10 has even less theoretical justification than does the linear relationship between D and Q. The generally accepted explanation of the experimental curve

$$D = a + b\rho_0 \qquad \rho_0 \geq 1.2 \text{ g./cc.} \tag{11}$$

where a and $b = (\mathrm{d}D/\mathrm{d}\rho_0)$ are constants, is that it results from the nonideal-gas behavior of the detonation products. Working from the definition of the adiabatic exponent

$$K = -\left(\frac{\partial \ln P}{\partial \ln V}\right)_{\text{constant entropy}}$$

Jones (18) showed that

$$\frac{\mathrm{d}D}{\mathrm{d}\rho_0} = \frac{D}{\rho_0}\left\{\frac{K+1}{2+\alpha} - 1\right\} = \frac{D}{\rho_0}(\epsilon - 1) \tag{12}$$

where

$$\epsilon = \frac{K+1}{2+\alpha}$$

$\alpha = [\partial\Delta E/\partial(PV)]_P$, and ΔE = the difference between the internal energy of the products and the potential energy of the explosive. The quantity ϵ is a measure of the nonideality of the gas products. For ideal gases, $\epsilon = 1$; for organic high explosives, its value may be as high as 2. The relationship between $(\mathrm{d}D/\mathrm{d}\rho_0)$ and the detonation energy is, from equations 3 and 12:

$$\frac{\mathrm{d}D}{\mathrm{d}\rho_0} = \frac{(\epsilon - 1)}{\rho_0}\sqrt{2Q(K^2 - 1)} \tag{13}$$

Since ϵ, K, and Q are all functions of ρ_0, and all vary from explosive to explosive, equation 13 makes any linear relationship between $(\mathrm{d}D/\mathrm{d}\rho_0)$ and Q most im-

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[4] Very few experimental values of the detonation velocity are known to within 2 per cent. Even the much studied RDX and TNT show more than this variation between measurements at the Naval Ordnance Laboratory, Picatinny Arsenal, and Los Alamos. Furthermore, detonation velocities of different explosives should be compared, not at the same absolute density, but at the same fraction of their crystal density. The very large effect of the volume fraction of air on the detonation velocity is shown in the well-known variation of D with loading density, but many investigators fail to compensate for this by making comparisons of explosives at the same air void content.

TABLE 3

Properties of pure explosives

Explosive	Name	Formula	Molecular Weight	Crystal Density	Oxygen Balance to CO	Constant-Pressure Heat of Formation $-\Delta H^{\circ}_{298}$
				g./cc.	*per cent*	*kcal./mole*
TNETB	Trinitroethyl trinitrobutyrate	$C_6H_6N_6O_{14}$	386.16	1.78	21	118.62 (27)*
PETN	Pentaerythritol tetranitrate	$C_5H_8N_4O_{12}$	316.15	1.78	15	125 (30, 38)
HMX	Cyclotetramethylenetetranitramine	$C_4H_8N_8O_8$	296.17	1.903	0	−17.93 (27)
RDX	Cyclotrimethylenetrinitramine	$C_3H_6N_6O_6$	222.13	1.802	0	−14.71 (27)
Tetryl	Trinitrophenylmethylnitramine	$C_7H_5N_5O_8$	287.15	1.73 (38)*	−8	−4.67 (34)
TNT	Trinitrotoluene	$C_7H_5N_3O_6$	227.13	1.651	−25	17.81 (34)
Explosive D	Ammonium picrate	$C_6H_6N_4O_7$	246.14	1.72 (38)	−13	97.04 (34)

* Reference.

probable. The linear relation of equation 10 is even less valid, and exceptions such as TNT (7) and TNETB (b = 3850 m.-cc./sec.-g.) abound.

V. EXPLOSIVES STUDIED

Table 3 identifies the pure explosives of this study and lists the values of their crystal densities and their heats of formation used in the computations. Density values, with the exceptions noted, were determined by the flotation method on microscopically selected, well-formed crystals. The heat of formation (the negative enthalpy of formation) is positive for heat evolved in the formation reaction. The sources of the values used are shown in the table. Several sources (23, 27, 30, 34, 38) are in fair agreement for most of the explosives, but an average value was chosen for PETN.

Computation of the energy of detonation may be illustrated with tetryl. The decomposition mechanism gives

$$C_7H_5N_5O_8 \rightarrow 2.5H_2O + 2.5N_2 + 5.5CO + 1.5C$$

Using the heat of formation of the products (29),

$$Q = \frac{10^3}{287.15}[2.5 \times 57.798 + 5.5 \times 26.416 - (-4.67) + 10.5 \times 0.592]$$

$$= 1047 \text{ cal./g.}$$

The last term in the original sum is the correction from constant pressure to constant volume conditions; this is $p\Delta v$ or ΔnRT, 0.592 times the number of moles of gas formed at 298°K. The convention of computing all heats of detonation at constant volume has been followed.

The mixtures used are identified in table 4. For those consisting of two explosives, each of which has zero or negative oxygen balance to carbon monoxide, the energy of detonation can be computed by simple additivity from the values for the pure explosives. For mixtures containing wax, the wax was treated as if it decomposed to carbon and hydrogen but underwent no further reaction. The wax was assigned a polymethylene formula $(CH_2)_x$, a density of 0.95 g./cc., and a

TABLE 4

Composition of mixtures and data from pressure computations

Explosive	Composition	Loading Density	Detonation Energy	Adiabatic Exponent *K*
		g./cc.	*cal./g.*	
Octol 77/23	HMX/TNT, 77/23	1.80	1167	2.91
Cyclotol 75/25	RDX/TNT, 75/25	1.70	1167	2.79
Cyclotol 60/40	RDX/TNT, 60/40	1.69	1119	2.75
Tetrytol 70/30	Tetryl/TNT, 70/30	1.64	1028	2.69
Picratol 52/48	Explosive D/TNT, 52/48	1.61	868	2.77
Compound B	RDX/TNT/wax, 59.4/39.6/1.0	1.68	1119	2.74
RDX/wax, 99/1	RDX/wax, 99/1	1.60	1216	2.72
RDX/wax, 95/5	RDX/wax, 95/5	1.64	1149	2.88
Composition A-3	RDX/wax, 91/9	1.60	1078	2.92
HMX/Wax, 91/9	HMX/wax, 91/9	1.71	1080	3.06
TNETB		1.70	1446	2.55
RDX		1.59	1228	2.70
Tetryl		1.63	1047	2.69
TNT		1.58	984	2.54
Explosive D		1.50	761	2.84

heat of formation of 5.5x kcal. This modification of the arbitrary mechanism was chosen to conform with the average effect of wax on the field performance of any explosive. This is an approximate treatment, since an underwater effects study of waxed series of various explosives gave evidence of a post-detonation reaction of a fraction of the wax with the detonation products. The late contribution due to this reaction is small, and its sign depends upon the oxygen balance of the organic explosive matrix and is predicted by the arbitrary water decomposition mechanism.

Table 4 also contains the values of the adiabatic exponent, computed by equations 2 and 3, for the loading densities shown. It can be seen that under the test conditions reported, the range in this exponent for all the test explosives is 2.54–3.06.

In addition to the explosives of tables 3 and 4, eight other pure explosives and three additional explosive mixtures have been tested, particularly for underwater and fragmentation effects. With one exception, the additional data confirm the relationships described below. The marked exception is for nitroguanidine (NQ), which exhibits distinctly less efficiency than that expected from its approximate energy of detonation (920 cal./g.) and its relatively high detonation velocity.

It is likely that NQ decomposes by somewhat different mechanisms from those of the other explosives and that its detonation energy is overestimated by the arbitrary mechanism. This possibility is supported by the presence of ammonia and the absence of carbon in the residue observed after detonation of this material.

Nitroguanidine is a good illustration of an explosive exhibiting a high detonation velocity (at comparable densities its rate is nearly that of RDX) and low detonation energy and pressure. This combination, particularly with the extreme contrast in the parametric values, is infrequent. A less marked example of such a combination is found in hydrazine mononitrate.

Of the unreported mixtures, pentolite (PETN/TNT, 50/50) is of interest because it consists of an explosive of negative oxygen balance (CO) mixed with one of positive oxygen balance (CO). For this case, different results are obtained if the arbitrary decomposition mechanism is applied: (*a*) as if the mixture were a single compound; or (*b*) as if the components of the mixture behaved independently. Contrary to the established practice, it was found that detonation phenomena required treatment (*b*), although long-time, nonpartitioned energy release, such as that measured calorimetrically, can be satisfactorily treated by procedure (*a*).

VI. SHAPED-CHARGE PENETRATION

The shaped-charge penetration test was made on charges cast or pressed over steel cones of 44 degree apex angle, $1\frac{5}{8}$ in. base diameter, and $\frac{1}{32}$ in. wall thickness. The prepared charge was a cylinder $1\frac{5}{8}$ in. in diameter and 4 in. long. Point initiation and tetryl boostering were used. The effect was measured by depth of penetration into a series of 1-in. thick, mild-steel plates at a 4-in. standoff distance.

This is a performance test at constant volume of explosive; a representative charge weight is 0.4 lb. Nine shots were made for each determination. The estimated precision is ±5 per cent of the measured penetration depth.

The data are presented in table 5 and figure 1. While direct proportionality can be shown between the measured penetration depth and a number of closely related parameters, the most physically significant seems to be the relationship to the detonation pressure shown in figure 1. The dashed lines outline the precision band for the depth measurements.

VII. FRAGMENT VELOCITY

The penetrating and damaging ability of shell fragments is indicated by their velocity. In the fragmentation test, the charges are cased in 5-in. long cylinders

TABLE 5

Shaped-charge penetration data for various explosives

Explosive	Loading Density ρ_0	Detonation Velocity†	Detonation Pressure	Shaped-Charge Penetration
	g./cc.	*m./sec.*	*kbar.*	*in.*
Octol 77/23	1.80	8539†	336	7.50
HMX/wax, 91/9	1.71	8682†	318	6.50
Cyclotol 75/25*	1.70	8134	297	6.24
RDX/wax, 95/5	1.64	8380	297	6.00
RDX/wax, 99/1	1.60	8061†	280	6.00
Cyclotol 60/40*	1.69	7843	277	6.17
Composition A-3	1.60	8228	277	5.83
Tetrytol 70/30	1.64	7310	238	5.12

* Cast charges.

† No correction was made for 1 per cent wax. Values for the first two charges were estimated from curves of RDX analogs.

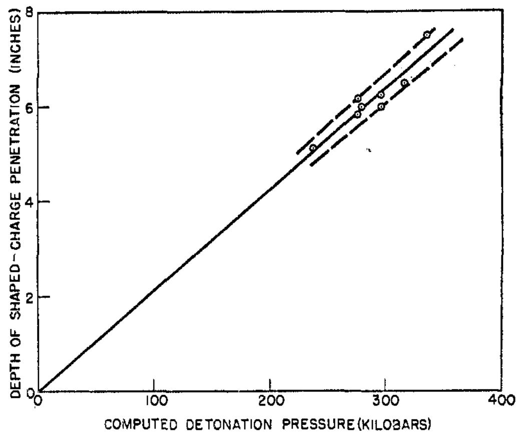

FIG. 1. Shaped-charge effect as a function of detonation pressure

TABLE 6

Data on fragment velocity for various explosives

Explosive	Loading Density ρ_0	Detonation Velocity D	Computed Detonation Pressure	Square of Fragment Velocity $\times 10^{-4}$
	g./cc.	*m./sec.*	*kbar.*	*(ft./sec.)*^{2}
TNETB	1.70	8142	318	2040
RDX	1.59	8026	277	1916
Tetryl	1.63	7400	242	1636
TNT*	1.58	6683	200	1360
Explosive D	1.50	6707†	176	1181
Cyclotol 75/25*	1.70	8134	297	1871
Composition B	1.68	7814	274	1836
Picratol 52/48*	1.61	6954†	207	1416

* Cast charges.

† Values for Explosive D and picratol 50/50 (15).

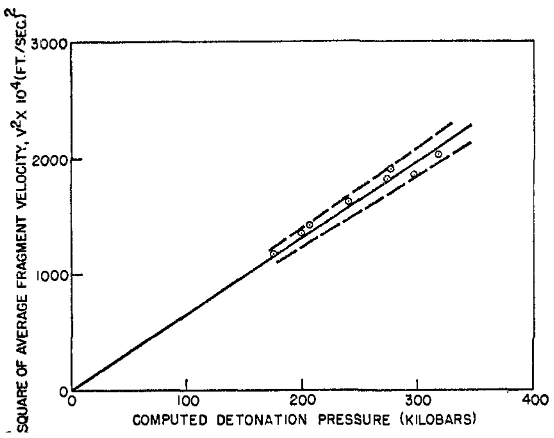

FIG. 2. Fragment velocity as a function of detonation pressure

of AISI 1045 seamless steel tubing, cold-rolled and stress-relief annealed, with a Rockwell hardness of about 100-B. The inside case diameter is about 2.00 in.; the wall thickness, 0.25 in. Velocities are measured 9 ft. away from the charge on all fragments in a selected beam. Values reported are average velocities.

This is a performance test at a constant value of the ratio of case weight to volume of explosive; a representative charge weight is 1 lb. Three to five shots were made for each determination, and the estimated precision is ±3 per cent to ±2 per cent of the average velocity found.

The fragmentation data and computed detonation pressures are given in table 6 and plotted in figure 2, which illustrates the direct proportionality between the square of the measured average fragment velocity and the detonation pressure. The precision band of figure 2 is ±6 per cent, since the square rather than the first power of the fragment velocity is involved.

VIII. AIRBLAST EFFECTS

Damage from airblast is, like all damage effects, a function of the target properties. Instead of using a standard target, the damage potential of airblast for any given target is customarily tested by measuring two free-air effects: peak pressure and impulse. The results are expressed as the equivalent weight of the explosive standard TNETB required to produce the measured effects. In general, charges are bare spheres of 1 to 10 lb. Peak pressure is measured by the shock velocity method (35); positive impulse is measured by using tourmaline and barium titanate gages calibrated for each shot by pressure values obtained by the shock velocity method. Data are obtained in the range 2 to 50 p.s.i. shock overpressure.

While the free-air tests are, like most explosive tests, conducted on an equal volume basis, they differ from the shaped-charge and fragmentation effects by showing extreme insensitivity to small variations in the loading density. Hence to avoid ambiguity, the results are reported on an equal weight basis.

Five shots were made for each determination. The estimated standard errors are ±3 per cent in equivalent weight for peak pressure and ±6 per cent in that for impulse.

The free-air data are given in table 7 and plotted in figures 3A and 3B, which suggest a direct proportionality between the equivalent weight and the detonation energy. However, the scatter is larger than that for the previous relations and one point on each curve, that for TNETB, marked No. 3 on the graphs, shows a decided departure from the trend exhibited by the other explosives. TNETB is the only material of this group containing an excess of oxygen over that necessary to form water and carbon monoxide; in fact, it contains enough oxygen to convert all the hydrogen to water and five-sixths of the carbon to carbon dioxide. Photographs of charges fired in air show turbulent mixing of the air and the detonation products. Measurements of free-air effects begin millireconds after the detonation, i.e., there is time available for post-detonation seactions sufficiently energetic to produce high-velocity disturbances which can overtake and contribute to the shock front. These facts collectively suggest that

TABLE 7

Free-air blast data for various explosives

Explosive	Computed Heat of Detonation	Free-Air Equivalent Weight Relative to TNETB	
		Peak presssure	Impulse
	cal./g.		
TNETB	1446	1.00	1.00
RDX/wax, 96.24/4.76	1153	0.97	1.17
Composition B	1119	1.04	1.05
RDX/TNT/wax, 66.62/28.62/4.76	1083	1.05	1.08
Composition A-3	1078	1.00	1.06
TNT	984	0.92	0.99
Picratol 52/48	868	0.83	0.92
Explosive D	761	0.78	0.80

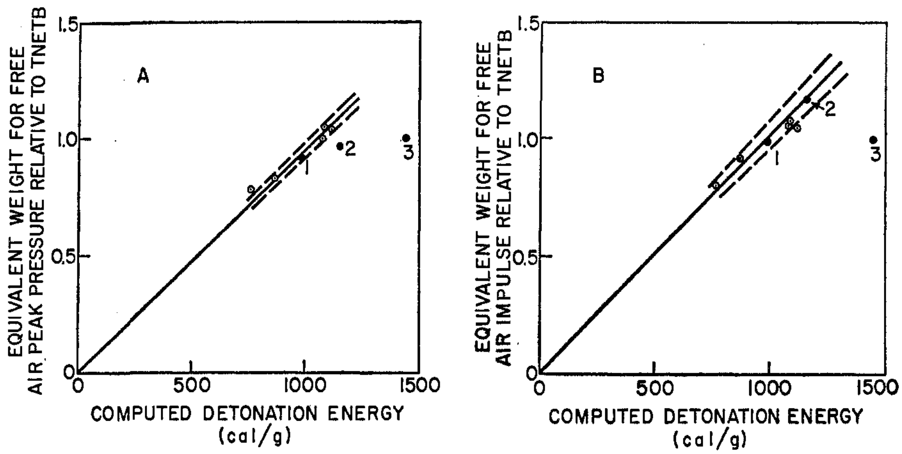

FIG. 3. Free-air equivalent weight as a function of detonation energy

the discontinuities of figure 3 are caused by the relatively large post-detonation reaction of the products with the oxygen of the air in every case except that of TNETB, the detonation products of which are already almost completely oxidized.

To test this possibility of contribution due to reaction with the atmosphere, three explosives of varying oxygen balance were selected. These were TNT, RDX, and TNETB, which are labelled 1, 2, and 3, respectively, in figure 3. Matle (21) has recently completed a careful study of these three explosives fired as 1-lb. spheres in balloons 4.5 ft. in diameter and containing various synthetic atmospheres. Table 8 contains his data for firings in nitrogen. Figure 4 clearly shows that in a nitrogen atmosphere both blast effects vary directly with the detonation energy. The firings in air measure, in addition, the afterburning contribution which is larger for the two explosives of lower oxygen content. Energy released by post-detonation reaction with air can, therefore, explain both the discontinuities and the scatter of figure 3.

TABLE 8

Blast data in nitrogen

Explosive	Formula of Explosive	Equivalent Weight Relative to TNETB		Computed Heat of Detonation
		Peak pressure	Impulse	
				cal./g.
TNETB	$C_6H_6N_6O_{14}$	1.00	1.00	1446
RDX/wax, 98/2	$C_3H_6N_6O_6/(CH_2)_n$	0.86	0.84	1196
TNT	$C_7H_5N_3O_6$	0.72	0.70	984

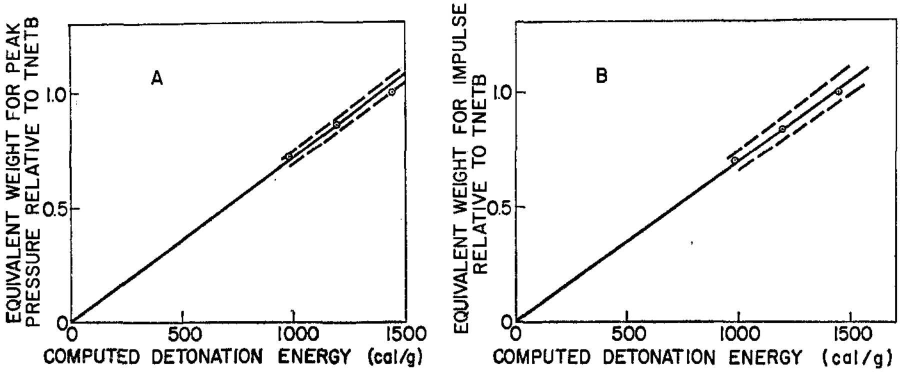

FIG. 4. Blast effect in nitrogen

Each relation of figure 4 can be used as a direct proportionality between the blast effect and the energy released to produce it. The effective energy is the detonation energy of the explosive plus any energy from a subsequent oxidation in air which is released rapidly enough to contribute to the blast effect. In this way, the oxidation contribution to the free-air blast of the other explosives of figure 3 can be estimated. Such estimates show that when a post-detonation contribution occurs, it is larger for the impulse than for the peak pressure effect, and in neither case is it equivalent to complete oxidation. This indicates that there is a longer time available for reaction which can contribute to the impulse than for that which can contribute to the peak pressure effect but that, in both cases, the time available for such reaction is less than that required for complete combustion. The total energy release in closed-chamber firings in air, on the other hand, approximates the heat of combustion of the explosive (14).

IX. UNDERWATER PHENOMENA

Underwater explosive effects are more complicated than those which have been discussed above. Excellent current reviews of the underwater explosion processes have been published (32, 33). The energy released by the detonation is partitioned into that in the shockwave, that dissipated in the water during travel of the shockwave from the charge to the gage(s), and that remaining in the oscillating bubble formed by the detonation products. Unlike the case of airblast, the boundary between the products and the medium is stable. As in airblast, the damaging potential is measured without use of a specific target. The underwater effects discussed here are shockwave and bubble energies.

The underwater data are reported as equivalent weights relative to pentolite. All charges were squat cylinders weighing about 1 lb. Firings were at a 9-ft. depth of water. Shockwave energy was calculated from deflection of a diaphragm gage (6) 3.5 ft. away and facing the side of the charge. Relative bubble energy is the ratio of the period constants cubed; period constants are determined by measuring the bubble period (6).

Five shots were made for each determination. The usual precision was ±0.02 unit in shockwave energy and ±0.05 unit in bubble energy.

For a given explosive, the underwater effects vary directly with the weight of the charge and hence, presumably, with the total energy released. For example, Cole (6) gives

$$E_s = kW^{1/3}\left(\frac{W^{1/3}}{R}\right)^{\delta} \tag{14}$$

where E_s = energy flux density,
W = charge weight,
R = distance from charge, and
k and δ are constants,

as the relationship between shockwave energy and charge weight. Both k and δ are specific for the explosive, but the variation for δ is small and, for practical purposes, δ may be considered as 2.00. Thus equation 14 shows direct proportionality between shockwave energy and weight for a given explosive. It also indicates that the fraction of the total energy in the shockwave at a given observation station (and hence also the fraction dissipated during the shock's travel to the station) is constant as the charge weight varies.

Comparison between explosives is far less simple than that between different weights of the same explosive. Table 9 contains the underwater data for some pure explosives as well as the estimated energies of detonation. Comparison of the measured shockwave energy with the detonation energy shows a roughly linear relationship between the two, but the curve does not extrapolate to the origin, i.e., direct proportionality does not exist. This indicates that the fraction of the total energy going into the shockwave varies from explosive to explosive; in more general terms, the energy partition is also a specific characteristic of the explosive. The dependence of the relative bubble energies of table 9 on the total (detonation) energy is very similar to the shockwave relation: roughly linear but not a direct proportionality. This is to be expected for shift in the energy partition from explosive to explosive.

Theoretical work has not yet reached the stage at which the energy partition can be predicted for the various explosives. Probably unavailable information about the kinetics of the detonation process as well as more reliable information

TABLE 9

Underwater performance data for various explosives

Explosive	Equivalent Weight Relative to Pentolite		Indices of Overall Performance		Computed Heat of Detonation
	Shockwave E_s	Bubble E_b	Product $I_p = E_s \cdot E_b$	Sum $I_s = E_s + E_b$	
					cal./g.
TNETB	1.18	1.16	1.37	2.34	1446
PETN	1.15	1.13	1.30	2.28	1416
RDX	1.10	1.02	1.12	2.12	1228
HMX	1.11	1.06	1.18	2.17	1222
Tetryl	1.00	0.98	0.98	1.98	1047
TNT	0.87	0.96	0.84	1.83	984
Explosive D	0.80	0.87	0.70	1.67	761
Cyclotol 75/25	1.04	1.01	1.05	2.05	1167
Cyclotol 60/40	1.02	1.00	1.02	2.02	1130

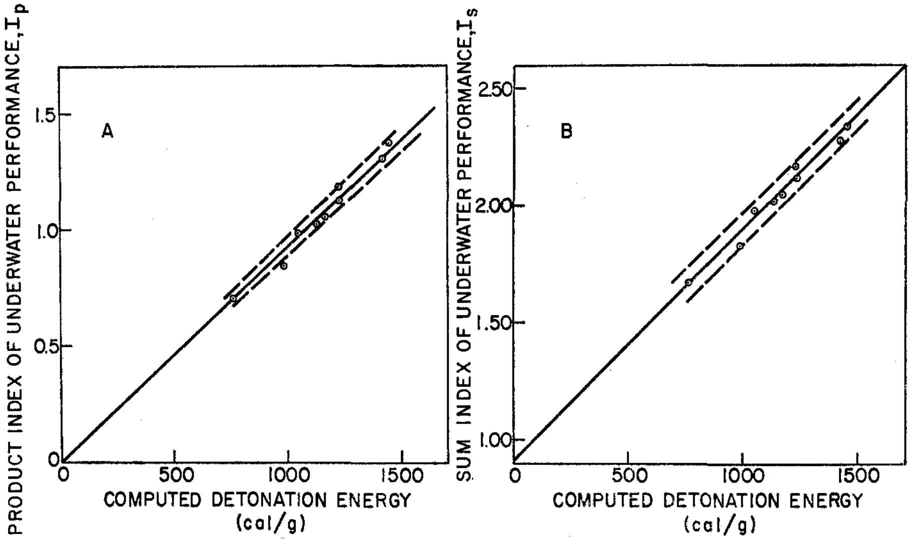

FIG. 5. Underwater index as a function of detonation energy

about the equilibrium products will be required. In the absence of such theory, the underwater data have been studied with the help of an arbitrary index of overall performance. Two such indices can be defined with equal weight assigned to each of the two measurements: the sum and the product of the two energies. Both indices correlate the data, within the experimental precision, with the detonation energy and both have been successfully used for empirical prediction. The product index automatically compensates for any absolute difference in the relative energy units used for the shockwave (E_s) and the bubble (E_b) energies. Moreover, as figure 5A shows, this index fortuitously shows a direct variation with the detonation energy.

According to figure 5A, the product index I_p is related to the detonation energy Q by the expression

$$I_p = CQ \tag{15}$$

where C is a constant. Now if x, y, and z are the partition coefficients, the detonation energy will be distributed as follows:

$$\underset{\text{Shockwave}}{xQ} + \underset{\text{Dissipated}}{yQ} + \underset{\text{Bubble}}{zQ} = \underset{\substack{\text{Total}\\\text{energy}}}{Q}$$

Hence

$$I_p = E_s \cdot E_b = xzQ^2/ab \tag{16}$$

where a and b are the constants necessary to convert the relative energy units of the shockwave and bubble, respectively, to absolute units. Equations 15 and 16 show that the choice of the observation station 3.5 ft. away from the 1-lb. charges has resulted in the relation

$$\frac{xz}{ab} = \frac{C}{Q}$$

In other words, the product of the partition coefficients for shock and for bubble varies inversely as the heat of detonation. It is, therefore, the choice of experimental conditions which produces the direct proportionality of figure 5A.

Figure 5B shows the variation of the sum index with detonation energy. Here

$$I_s = \frac{xQ}{a} + \frac{zQ}{b}$$

and it is the nature of the variation of x and z from explosive to explosive as well as the choice of standard explosive which results in the linear relation of figure 5B. This graph illustrates a practical point that is less obvious in figure 5A: the increase of underwater effectiveness is a very small part of the increase in detonation energy.

X. GENERAL DEPENDENCE OF EFFECTS ON EXPLOSIVE PROPERTIES

The present work has shown that, for organic explosives near their voidless density, the close-in effects (shaped-charge and fragmentation) vary directly with detonation pressure, whereas the more distant effects (airblast and underwater) depend primarily on total detonation energy. The data can also be used to show that the third detonation parameter, detonation velocity, is of little use in correlating the effects by itself although it is, of course, essential in defining the relationships between the other two detonation parameters. For instance, a simple plot of detonation pressure against detonation energy will not reveal quantitative relationships such as those of equations 2 and 3.

Because all of the effects considered can be shown to be related to two detonation parameters, and the two parameters are related to each other, it follows that the effects are also rationally related to one another.[1] The relationship between effects will not generally be revealed by simple intercomparison because of the complexity of the interdependence of the detonation parameters and because of the confusion introduced by environmental contributions to the effects, e.g., post-detonation reaction with air.

The present results must, of course, be restricted to the relatively nonporous charges of organic explosives under the test conditions described. They serve to illustrate the type of relationships to be expected for different conditions and to forecast the more exact relations to be expected when a true equation of state and rigorous equilibrium computations are available for determining detonation energy and pressure.

A less obvious restriction on the present study is the kinetics of the explosives considered. The damage tests have been arranged approximately in the order of the time available for the energy released by the chemical reaction to contribute to the effect. From photographic studies of fragmentation, it is known that the casing was fragmented 15 microsec. after initiation. Hence the chemical reaction of 1 lb. of explosive and the energy transfer causing the observed fragment velocity must have been completed in about this time interval. Jet formation in the shaped charge is believed to be an even more rapid phenomenon. In the case of airblast, arrival time of the shock at the first gage (about 6 feet from a 1-lb. charge) is about 2000 μsec. For underwater shock, the arrival time at the diaphragm gage (3.5 ft.) is about 650 μsec. Not all of this travel time is available for effective post-detonation reaction, since the charges also obey the scaling law. But even a small fraction of the travel time (say 10 per cent) results in an appreciable increase over the fragmentation effect in available reaction time. The expansion time of the underwater bubble from a 1-lb. charge is about 200,000 μsec. Again, only a fraction of this time is available for reaction, because the mixture cools rapidly as the gas expands. However, there is certainly a longer reaction time available than is the case for the shock. Since the explosives investigated exhibited the same energy release for the slowest and the fastest of the effects, it follows that these explosives reacted sufficiently rapidly to have completed the decomposition in every case. The relationships found depend on this rapidity of reaction and cannot be expected to hold for a more slowly acting explosive, e.g., an explosive mixture containing an inorganic oxidizer such as ammonium nitrate.

XI. SIMPLE ADDITIVITY OF EFFECTS

From the nature of the relationships found it would be expected that the properties of a mixture of conventional organic explosives could be predicted from the measured properties of its pure components. The detonation energy and the effects dependent on it should be predictable by a simple additivity rule. The detonation pressure is, by equations 2 and 3,

$$P = 2(K - 1)\rho_0 Q$$

Since $\rho_0 Q$ is detonation energy per unit volume, it follows an additivity rule on a volume fraction basis. Hence if the adiabatic exponents of the various components are near the same value, detonation pressure would also follow the additivity rule.

Properties of mixtures can be predicted by the simple additivity rule:

$$A = \sum_i x_i A_i$$

where A is the property per gram (cc.), x is the fraction by weight (volume), and i is the component index. Except for the shaped-charge effect in which data on the pure components are lacking, all mixture effects measured in the present work confirmed the simple additivity rule. In fact, the rule also holds within 0.3 per cent for predicting the detonation velocity of the cyclotols (7) at their voidless density but less well at lower densities. It has also been found applicable for the detonation velocity of other mixtures at voidless density, although the theoretical equations indicate a quadratic relationship which would also include the adiabatic exponent K. Applications to detonation velocity should therefore be made cautiously.

The use of the additivity principle has been suggested before—particularly in empirical applications to detonation velocity. Its broad applicability is, however, apt to be overlooked. It is emphasized here both as a helpful guide in planning experimental work and as an incentive for obtaining more effects data on pure explosives in contrast to the less efficient and more frequent emphasis on practical mixtures.

Many members of the Chemistry Research and Explosions Research Departments cooperated not only in collecting the data but also in critical discussion of their handling and interpretation. In several instances, experimental programs were expanded to increase the value of the study. For all of this assistance, the writer is very grateful. Special acknowledgment should be made of the contributions of E. A. Christian, N. L. Coleburn, E. M. Fisher, and C. C. Matle.

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