

Calorimetric Determinations of the Heat and Products of Detonation for Explosives: October 1961 to April 1982

D. L. Ornellas

April 5, 1982

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CONTENTS

Abstract	1
Introduction	1
Experimental	2
Apparatus	2
Operation	3
Calibration	5
Detonation	5
Heat Measurement	7
Product Analysis	8
Explosive Materials	9
Results and Discussion	10
Theoretical Calculations and their Interpretation	10
Experimental Results	13
Amatols, Ammonium Nitrate/TNT	13
1-Ammonium-3,5-dinitro-1,2,4-triazole (ADNT) and Ammonium Nitrate (AN)/ADNT	19
Benzotrifuroxan (BTF)	21
1,2-Bis(difluoroamino) Perfluorocyclobutane (BDFPCB)/ Tris(difluoroamino) Perfluorobutane (TDFPB)	23
BDFPCB/TDFPB/Al	23
1,2-Bis(difluoroamino) Propane (1,2-DP)	25
Bis(2,2-dinitro-2-fluoroethyl) Formal (FEFO)	28
Bis(trinitroethyl) Adipate	29
Bitetrazole	32
Bitetrazole with Hydrazine Nitrate and Bitetrazole with Benzotrifuroxan	33
Composition B (Comp B)	34
Cyclotetramethylene Tetranitramine (HMX)	36
Cyclotrimethylene Trinitramine (RDX)	39
Ethylene Diamine Dinitrate (EDN)	39
Ethylene Diamine Dinitrate/Ammonium Nitrate/RDX (EAR)	40
Ethylene Diamine Dinitrate/Ammonium Nitrate/RDX/Aluminum (EARL-1)	43
Hexanitrobenzene (HNB)	45

Hexanitrostilbene (HNS-II)	46
Hydrazine Nitrate (HN)	48
Hydrazine-Hydrazine Nitrate Explosives	48
LX-04-1	50
LX-11-0	52
Nitromethane (NM)	52
Nitromethane/Nitropropane/Ethylenediamine	54
Octol	55
Pentaerythritol Tetranitrate (PETN)	57
RX-04-DS	61
RX-08-EP	63
RX-22-AG	64
RX-25-BF	66
RX-36 Explosives	67
Tetranitromethane/Aluminum (TNM/Al)	69
Tetranitromethane/Carbon (TNM/C)	71
Triaminotrinitrobenzene (TATB)	71
2,4,6-Trinitrotoluene (TNT)	72
XTX-8003 (Extex)	78
References	81

**CALORIMETRIC DETERMINATIONS OF THE HEAT AND PRODUCTS OF DETONATION
FOR EXPLOSIVES: OCTOBER 1961 TO APRIL 1982**

ABSTRACT

This report is a compilation of heat-of-detonation and product-composition data obtained at Lawrence Livermore National Laboratory during the last 21 years. In each determination, a 25-g high-explosive charge was detonated in a bomb calorimeter; a complete calorimetric measurement was made in 1 to 2 h with a precision of 0.3%. Data were interpreted using thermodynamic and hydrodynamic computer calculations. For unconfined or lightly confined charges, the released energy is largely retained in the products, which are subsequently shocked considerably off the Chapman-Jouguet isentrope by reflections from the bomb wall. For heavily confined charges, the detonation energy is largely converted to kinetic and internal energy of the confining case, and the products expand with minimal reshock along the Chapman-Jouguet isentrope.

INTRODUCTION

Precise fundamental information about the detonation process and its chemistry can be obtained by combining calorimetric measurements with product analysis of appropriately designed experiments. Although energy release and product composition at the Chapman-Jouguet (CJ) condition cannot be measured in a calorimeter, these values can be measured over the freeze-out region on the CJ isentrope. Observed heats and product compositions have been used

- To demonstrate the suitability and range of applicability of thermodynamic-hydrodynamic codes that predict explosives performance,
- To determine the role of diffusion at the intra- and intermolecular levels,
- To provide information for nonideal explosives on the partition of energy between the detonation front and product expansion adiabat and demonstrate that the composition and particle size of the high explosive can affect the shape of the adiabat.

Discussions of specific aspects of these effects have been published elsewhere.¹⁻⁴

EXPERIMENTAL

APPARATUS

Figure 1 shows the calorimetric system used for these measurements. The spherical bomb (K), made of 3.2-cm-thick 347 stainless steel or 400 Monel (depending on the explosive used), had an i.d. of 21.6 cm and an internal volume of 5.28 litre. The 9-cm opening was covered by a lid 3.8 cm thick at the center. The lid was secured by 12 1-cm-diam stainless steel bolts inserted through the lid flange and sealed with a Neoprene O-ring. The bomb and lid weighed 52 kg.

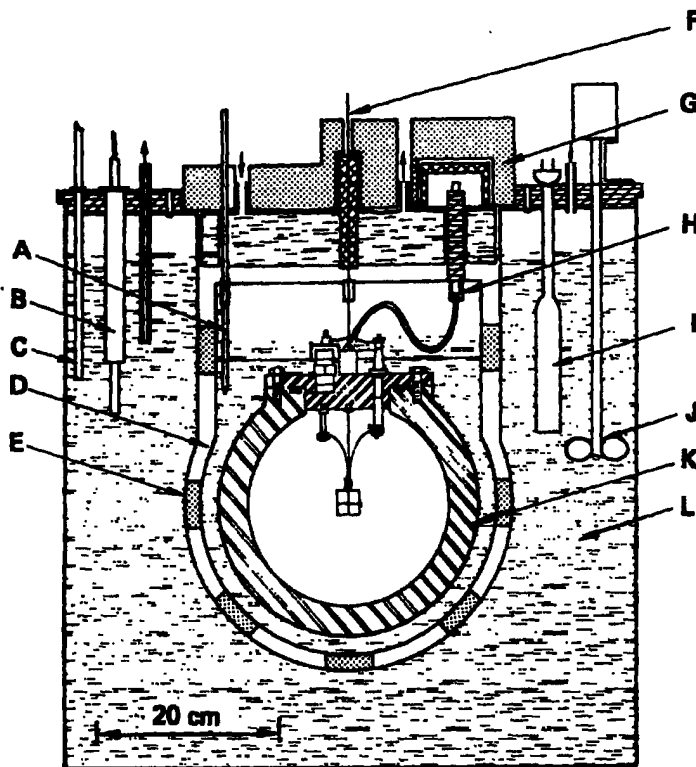


Figure 1. Calorimeter. A, quartz thermometer; B, nickel resistance thermometer; C, mercury-in-glass thermometer; D, calorimeter bucket with lid; E, Styrofoam support blocks; F, support cable; G, Styrofoam insulation; H, firing-lead connector; I, knifeblade heater; J, stirrer; K, bomb; and L, constant-temperature jacket.

The bomb was suspended by a 0.16-cm-thick braided steel cable (F) in a polished stainless steel calorimeter bucket (D) that held 8.4 kg of water; the water was stirred by vertical oscillations of the bomb. The bomb and spherical portion of the calorimeter bucket were separated by 1.8 cm of water. The water temperature was sensed by a quartz thermometer probe (A).

The calorimeter was surrounded by a constant-temperature jacket (L) with a jacketed lid. An insulated firing-lead connector (H) was mounted through the bucket lid and extended through a well in the jacket lid. Small Styrofoam blocks (E) supported the calorimeter bucket inside the jacket and provided an air gap of 1.3 cm between the bucket and the inner walls of the jacket. The constant-temperature jacket was maintained at $25.000 \pm 0.001^\circ\text{C}$ by a temperature controller that sensed the temperature using a nickel resistance thermometer (B) and heated using a knifeblade heater (I). A small centrifugal pump (not shown) circulated water from the jacket through the jacket lid.

Figure 2 shows the bomb lid (I) in detail. The bomb was suspended at the lifting block (H) during operation and when moved into or out of the calorimeter. Valve (B) permitted pressurization or evacuation of the bomb. Firing current passed through the insulated high-voltage terminal (G), and cap (A) on valve (B) served as a grounding terminal. The exposed surfaces of the high-voltage terminal were made of mica and stainless steel to avoid reaction with the detonation products. O-rings were used to seal the valve and terminal.

Stirring by vertical oscillation of the bomb was chosen as a convenient way to keep the energy equivalent of the system low. The stirring rate was 25 cycles per min; higher stirring rates caused splashing and loss of calorimeter water. A 6.4-cm stroke forced about half the water in the bucket past the bomb with each stroke.

The thermometric system was a Hewlett-Packard Model 2801A quartz thermometer with a sensitivity of 10^{-4}°C for differential measurements. It had direct digital readout and was easily calibrated. The thermometer was interfaced to a Digital Computer Controls, Inc., D-112 computer.⁵

OPERATION

To begin operation, the calorimeter bucket was filled with 8.4000 ± 0.0005 kg of distilled water and the water temperature adjusted so

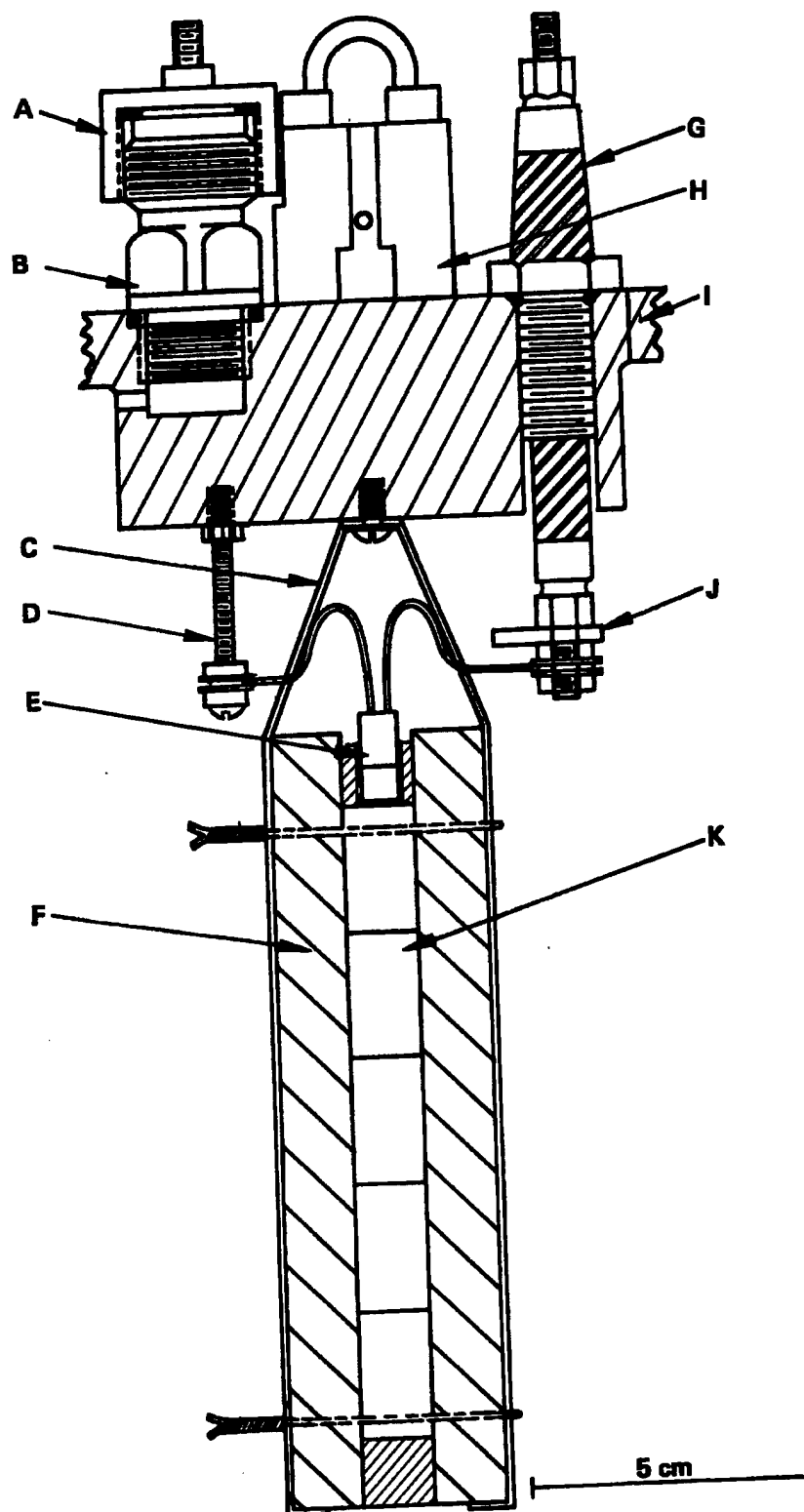


Figure 2. Calorimeter bomb lid with confined charge. A, valve cap; B, valve; C, gold support straps; D, ground terminal; E, detonator; F, gold cylinder; G, high-voltage terminal; H, lifting block; I, bomb lid; J, terminal shield; and K, explosive charge.

that the final calorimeter temperature was very near the jacket temperature. An equilibration period of 0.5 h was allowed before temperature measurements were started.

Calibration

We determined the energy equivalent of the system by burning about 5.9 g of benzoic acid (certified by the National Bureau of Standards) with purified oxygen at a pressure of 30 atm in a platinum crucible. The benzoic acid was pressed at 140 kg/cm^2 into a pellet 2.54 cm in diameter and about 1.3 cm high. The 0.05-cm-thick crucible was suspended in the same position as the explosive charge (Fig. 1), and 15 ml of water was placed in the bomb to conform with standard benzoic acid calibration conditions. The benzoic acid was ignited by an electrically heated 14-cm length of 0.015-cm-diam pure iron wire. The heat input from benzoic acid was corrected to standard states.⁶ Total corrections amounted to 0.1%.

For each calibration, we calculated the thermal equivalent of the standard instrument, defined as the calorimeter bucket containing 8400.0 g of water and the bomb without calibration hardware and materials. We also corrected the thermal equivalent value for erosion of steel from the bomb walls and for deposition of gold and platinum that took place during each detonation experiment.

The thermal equivalent of the instrument, taken as the average of six calibration runs, was $15,200 \pm 4 \text{ cal/}^\circ\text{C}$. This error of $\pm 0.03\%$ indicated the ultimate precision of the instrument.

Detonation

Figure 1 shows the experimental arrangement used for detonation work with unconfined charges; unconfined charges were suspended at the center of the bomb by a fiberglass-tape stirrup. Fiberglass string tied around the stirrup and the charge held the assembly together. Figure 2 shows the arrangement used for work with heavily confined charges. The charge (K), confined in a gold cylinder (F), was suspended by two gold straps (C) attached to the lid. Gold wires tightened around the straps and the gold cylinder held the cylinder in place on bent ends of the straps. The confining cylinder was closed on both ends and extended a distance of one charge diameter beyond both

ends of the charge. (Explosive charges were typically 12.7 mm in diameter and 114 mm long.) The confining cylinders typically had a wall thickness equal to the charge diameter.

The optimum configuration which allows isentropic expansion of detonation products and for which end effects are negligible is an infinitely long, heavily confined, open-ended charge. However, charge length was limited by the calorimeter dimensions; end effects were not negligible because some detonation products that jetted from the open ends of the confining cylinder were shock-reheated by collision with the bomb wall and reequilibrated. Reequilibration of these products can be avoided by confining the ends of the charge. However, end confinement presents the undesirable possibility that reflections generated by a head-on detonation impinging against the ends of the gold cylinder may shock some products to a state above the CJ isentrope.

We fired heavily confined NM charges (Table 29) and TNT charges (Table 45) with and without end confinement to investigate the magnitude of this effect. The experiments with end confinement showed an increase in the heat of detonation and, when the two isentropes were compared at the same volume, showed an increase in the species representative of a lower-temperature isentrope ($C(s)$, H_2O , and CO_2) and a corresponding decrease in the species representative of a higher-temperature isentrope (CO and H_2).

This evidence indicated that the undesirable effect of end confinement was very small and that products from charges having end confinement were more nearly representative of those along the CJ isentrope than products from charges not having end confinement. For this reason, we adapted heavy end confinement to our standard configuration as described above.

Because the bottom of the bomb was most damaged by high-velocity gold fragments, it was protected by two stainless-steel discs 6.4 mm thick and 64 mm in diameter.

To contain liquid explosives under vacuum conditions, we sealed the gold cylinder 12.7 mm from the top end with a translucent laminate film of 0.025-mm polyethylene and 0.013-mm Mylar. A vacuum-tight seal was obtained by compressing the film between appropriately machined gold surfaces. The weight of film averaged 0.017 g per experiment. The film also isolated the main-charge liquids from the PETN booster, thus avoiding possible chemical interactions. The bottom of the gold cylinder was sealed by electron-beam welding the gold plug in place.

Detonators (E, Fig. 2), were fabricated as follows: bare 0.08-cm-diam platinum leads were cast in an alumina body that was then sintered at 1400°C. A 0.05-mm-diam gold bridgewire was soldered between the leads. The detonator cup (6.4 mm i.d. and 10 mm long) was spun from 0.25-mm-thick gold sheet and attached to the alumina body using small amounts of contact adhesive. About 100 mg of powdered PETN was packed around the bridgewire in the detonator cup, and a 150-mg high-density (1.71 g/cm^3) pellet of PETN was placed next to the main charge. In some cases, the face of the gold cup was removed so that the high-density pellet was in direct contact with the main charge. Because of differences in the initiation characteristics of the explosives studied, boosters of various sizes were sometimes required. Boosters were made of PETN with a density of 1.71 g/cm^3 , and their weight was kept to a minimum. The heat and products of detonation of each explosive were corrected for the PETN used in the detonator and booster.

Before firing the explosive, the bomb was evacuated to a pressure of about 50 $\mu\text{m Hg}$. To avoid splashing of the water in the bucket, firing was initiated when the bomb was at the bottom of its stirring stroke. Detonators were fired using a 6.72 μF -2400 V capacitance-discharge unit.

Heat Measurement

Temperatures were read every 10.5 s by the quartz thermometer. The computer program checked the foredrift and afterdrift for linearity, indicated when to fire, terminated the measurements when complete, and calculated the corrected temperature rise using the Regnault-Pfaundler method.⁷ The main period was about 20 min long for unconfined experiments and about 60 min long for heavily confined experiments; the foredrift and afterdrift periods were each about 20 min long.

The equal-area time is the time at which the areas above and below the time-temperature curve are equal. The temperature rise was such that the equal-area time for both combustion and detonation occurred about 2.4 min after ignition. Expressed as a percentage of the total temperature rise, the temperature rises at the equal-area time were $62.9 \pm 0.6\%$ °C for calibrations and $63.6 \pm 0.8\%$ °C for detonation experiments. The close agreement of these values indicated that the overall thermal-transfer conditions in a calibration run closely approximated those of a detonation experiment.

To determine the heat produced in a detonation experiment, the energy equivalent of the standard instrument was corrected for the platinum, gold, alumina, stainless steel, and explosive used in the experiment as well as for the metals deposited and steel eroded from preceding experiments. The total energy produced was then corrected for water vapor in the bomb, energy input of the bridgewire, pressure-volume work done by the gases, and the contribution from the PETN in the initiator system. Dividing the corrected total energy by the weight of the explosive gave the heat (enthalpy) of detonation per gram of explosive.

Product Analysis

A vacuum system was built to measure total volume of gaseous detonation products and to permit the taking of samples. Gases were transferred from the bomb into the system by expansion of the gases and pumping. To help remove the gaseous detonation products, the bomb was heated to 100°C at the end of the transfer. Water was condensed in two in-line traps at -95°C and determined gravimetrically. Ammonia that was not retained in the water traps reacted with sulfuric acid in a third trap.

The remaining gases were pumped into a calibrated 35-litre stainless steel tank where the pressure and temperature were measured. The tank contained small Teflon spheres that assured complete mixing of the gases when the tank was tumbled. Carbon dioxide, carbon monoxide, nitrogen, hydrogen, methane, and, occasionally, depending upon the explosive, smaller amounts of ethane, acetylene, cyanogen, formaldehyde, nitrogen oxides (N_2O , NO , NO_2), and carbon tetrafluoride were determined quantitatively by mass spectrometry. The amounts of the minor products (methane, ethane, acetylene, and formaldehyde) were sometimes checked by chromatographic methods.

While the bomb was still hot, the interior was washed with water. Ammonia was determined by wet analyses of the two water traps, the sulfuric acid trap, and the bomb washings. Hydrogen cyanide was determined by wet analyses of the water traps and bomb washings. Small amounts of CO_2 and occasionally, depending upon the explosive, nitrite ion (NO_2^-) and nitrate ion (NO_3^-) were found in the water traps and bomb washings; these species were determined by wet analyses.

For explosives that produce hydrogen fluoride and little or no water, two traps for HF and water having either polyethylene or Kel-F residence areas

and made with Monel valves and tubing were substituted for the glass water traps. Both traps contained potassium fluoride that was prepared by heating it in air at 475°C. These traps were held at -130°C during the gas transfer. The HF was determined by wet analysis of the contents of these traps and the Monel bomb washings.

The solid products that are water insoluble--silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and carbon (C(s))--remained in the bomb and were determined by difference using the material balance. The solid products were amorphous. The presence of SiO_2 was established by infrared spectroscopy. More than half of the carbon was recovered by filtering the bomb washings. This solid residue was dried and analyzed for C, H, and N. Typical analyses were C: 25-45%, H: 0.25-1.0%, and N: 1-15%. This accounted for most of the nitrogen and hydrogen missing in the material balance of all explosives that produced C(s) as a product. The remainder of the residue was mainly finely divided gold and a smaller amount of alumina from the detonator body. None of our attempts to identify the form in which this hydrogen and nitrogen exist in the solid residue have been completely successful. We do have unpublished information⁸ indicating that it is not unusual for carbonaceous materials to hold hydrogen and nitrogen in interstitial spaces at temperatures up to 1900°C.

High-order detonation was usually verified by visually inspecting the interior of the bomb to determine the condition of the gold fragments and by the sound detected at the time of firing.

Explosive Materials

We studied PETN first because we used it in the detonator and booster for nearly all subsequent studies. Therefore, a reliable heat-of-detonation value and a knowledge of product composition were essential. Another reason for studying PETN first was that this explosive is relatively oxygen-rich and yields no solid products, which simplified the product analysis.

High-density charges were pressed as right cylinders in mechanical dies at pressures of 1000-2000 kg/cm^2 , with or without vacuum, and at temperatures ranging from ambient to 120°C, depending upon the explosive. Pressed pieces were usually 12.7 mm long.

RESULTS AND DISCUSSION

THEORETICAL CALCULATIONS AND THEIR INTERPRETATION

Hydrodynamic codes were used to calculate the energy distributions of PETN between detonation products, the metal confinement, and the calorimeter wall as a function of time. The KO code,⁹ a one-dimensional hydrodynamic code, was used for calculations on 25.4-mm-diam unconfined or lightly confined charges. Charges of this diameter were about 28.0 mm long and approximated the spherical model used in the calculation. The HEMP code,¹⁰ a two-dimensional hydrodynamic code, was used for calculations on heavily confined charges. These charges were several times longer than their diameters, and one-dimensional calculations do not take end effects into account.

Figure 3 shows the results of the one-dimensional hydrodynamic calculations on unconfined PETN charges. Released chemical energy is largely retained in the products, and only 9% is transferred to the wall by shock mechanisms. As shock reverberations occur in the bomb, the energy remaining in the products is converted alternately to kinetic energy and internal energy. When reverberations end, the products occupy the full volume of the bomb. The remaining energy is transferred to the wall mainly by conduction.

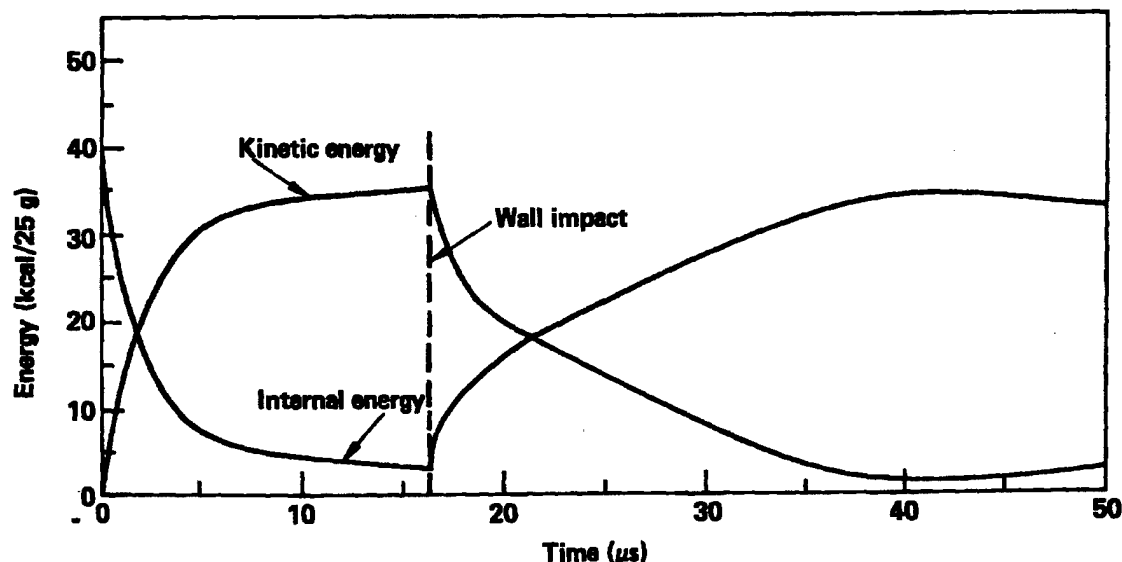


Figure 3. One-dimensional hydrodynamic calculations for unconfined PETN charges showing energy history of products.

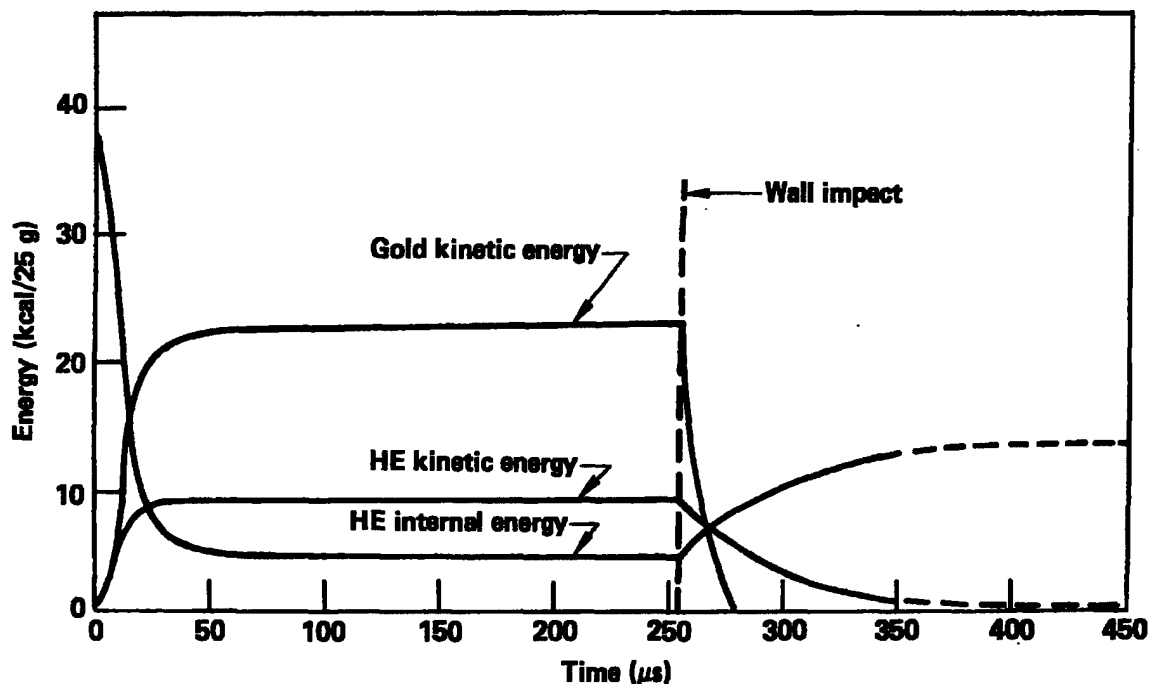


Figure 4. Two-dimensional calculations for confined PETN charges (12.7-mm-diam gold cylinder with unconfined ends) showing energy history of products and confining metal.

Figure 4 illustrates the results of two-dimensional calculations (extrapolated beyond 50 μ s by one-dimensional calculations) on 12.7-mm-diam heavily confined PETN charges with unconfined ends. About 67% of the released chemical energy is converted to kinetic and internal energy of the confining metal. For longer 6.4-mm-diam heavily confined charges, end effects decrease; about 75% of the released chemical energy is transferred to the confining metal. The energy transferred to the confining metal is not available to the detonation products and is transferred to the calorimeter walls.

The low-pressure portion of the CJ isentrope in the pressure-volume plane is shown in Fig. 5. The calculated off-isentrope positions to which the products are shocked by reflections from the bomb wall are also indicated on this graph. Products from unconfined charges are shocked to an energy state considerably above the CJ isentrope, whereas products from heavily confined charges receive much less shocking and expand essentially along the CJ isentrope. The vertical line drawn at a constant-volume ratio of 370 represents the ratio of V , the volume of the bomb, to V_0 , the volume of 25 g of PETN at initial density. When shock reverberations have ended, the

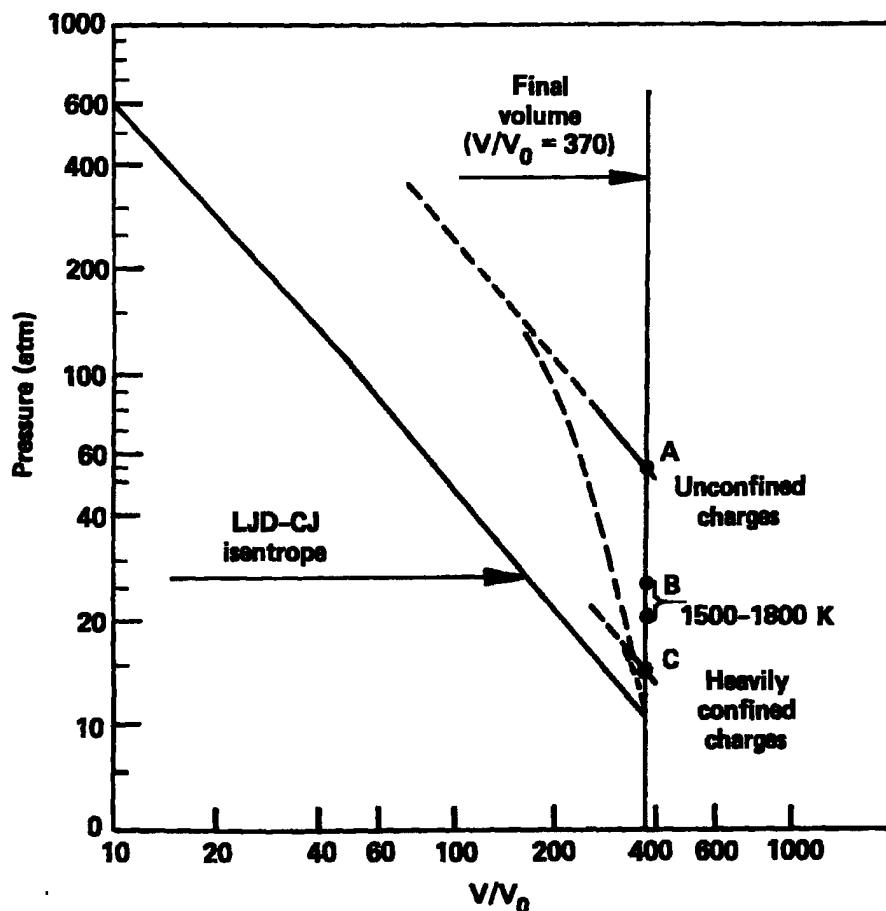


Figure 5. Chapman-Jouget (CJ) isentrope for PETN showing calculated hydrodynamic history of detonation products. A, unconfined charges; B, heavily confined charges (12.7-mm-diam gold cylinder); and C, heavily confined charges (6.4-mm-diam gold cylinder). Charges B and C were not confined at the ends.

condition of the products may be represented by a point somewhere along this constant-volume cooling line, regardless of the shock history of the products.

Peak shock conditions for the products from unconfined charges are calculated to be of 100 to 300 atm pressure at about 4500 K; after reverberations have ended, the conditions are 50 atm at about 3500 K. The calculated peak shock conditions for the products from heavily confined charges are very nearly the same as those prevailing after reverberations have ended: about 25 atm and 1700 K for the 12.7-mm-diam charge (point B, Fig. 5) and about 20 atm and 1400 K for the 6.4-mm-diam charge (point C, Fig. 5). Compared with the products from confined charges, those from unconfined charges are at low pressures and very high temperatures.

In summary, studies^{1,11-13} indicate that the detonation products from long cylindrical heavily confined charges are those found on the CJ expansion isentrope in the freeze-out range; for most CHNO explosives, the composition is frozen within the approximate temperature range of 1500 to 1800 K. These studies also indicate that the products from unconfined charges are shocked considerably above the CJ isentrope, re-equilibrate under conditions of high temperature and relatively low pressure, bear no quantitative resemblance to those found on the CJ isentrope, and can be calculated using the ideal-gas equation of state. Accordingly, we refer to the results from heavily confined charges as ΔH detonation and those from unconfined charges as ΔH reaction.

EXPERIMENTAL RESULTS

The following tables list the corrected results and experimental conditions. Unless otherwise noted, charges are 12.7 mm in diameter and 114 mm long; results are corrected for the PETN used in the initiation system. All errors are double the estimated standard deviation of the mean and are based, in part, on results for other explosives for which more than two experiments were conducted. Unless otherwise noted, one experiment was performed. Each set of tables is accompanied by the rationale for conducting the experiment, an interpretation of results when appropriate, and conclusions. When possible, we also include a description of the type, purity, and analyses of each explosive studied. The ΔH detonation calculated from the observed products use heat of formation data taken from the JANAF Tables,¹⁴ with the exception of the value for ΔH_f° 298 for carbon, which was given a value of +8.75 kcal/mol to account for the highly disordered form that carbon exhibits in detonation products. The material recoveries given in the tables do not include solid carbon.

Amatols, Ammonium Nitrate/TNT

Rationale. Performance of an explosive is a function of both the peak energy released near the detonation front and the remainder of the energy that is released during the Taylor wave. The partitioning of energy between the front and the expansion (and the rate of energy release in the latter) is controlled by either chemical, kinetic, or diffusion processes.

We used detonation calorimetry to investigate these processes. We prepared formulations of ammonium nitrate (AN) and TNT in which the relative proportions, particle size of the AN, and charge density were varied; we then determined the total energy released and quantitatively analyzed the detonation products. Isotopic labeling of one of these compositions with ^{15}N was also used to give additional insight into the reactions, i.e., the amount of nitrogen mixing that takes place between two explosives, that occur in or near the reaction zone. Reference 4 gives further details.

Experimental. Flake TNT, Military Specification, Grade III, was used. AN was prepared by grinding commercial prilled AN (minimum 97.6 wt% AN containing 0.4 to 0.9 wt% parting agent) in a ball mill and sieving to separate particle sizes. The particle-size distribution was determined using a Quantimet-QTM 720 Image Analyzer. Mass spectrometry showed that isotopically labeled AN samples contained 99+% ^{15}N . All AN samples were stored in a desiccator at all times.

The formulations were prepared by slurring the required amount of AN in a solution of TNT in dry toluene and evaporating the toluene. The cake of explosive was then crushed to pass through a 30-mesh sieve, blended, and pressed into pellets to about 95% of theoretical maximum density (TMD).

Isotopic labeling of A^{15}N was used in two experimental configurations with 20/80 amatol. In both configurations, the TNT was unlabeled. In the first, all of the $^{15}\text{NH}_4^{15}\text{NO}_3$ was labeled and uniformly distributed throughout the charge. In the second, the 12.7-mm-diam charge had a 6.35-mm-diam core containing uniformly distributed A^{15}N amatol inside an annulus (6.35-mm i.d. and 12.7-mm o.d.) of AN having normal isotopic distribution. The purpose of the second configuration was to determine if the reaction zone was uniform across the diameter of the charge. The AN particle sizes were the same for both configurations.

Results and Discussion. The data in Table 1 indicate that the total energy of the system is not highly dependent on the ratio of AN to TNT, the AN particle size, or the charge density. Although the wt% of AN ranged from 20 to 81%, the experimental values differ by less than 10%; similarly, the formulation fired at 52% of TMD (column 6) gave results comparable to the five samples fired at 95% TMD. For charges at the same % TMD (columns 1-5), it seems that although increasing amounts of AN increase the detonation energy by oxidizing

Table 1. Heats and products of detonation of amatols as functions of composition, ammonium nitrate particle size, and charge density.

Experimental conditions	1	2	3	4	5	6
Composition (AN/TNT), wt%	9.7/80.3 ^a	58.7/41.3 ^{b,c}	61.4/38.6 ^{c,d}	60.3/39.7 ^{c,e,f}	81.1/18.9 ^{f,g}	61.4/38.6 ^{c,d}
AN particle size (W/50), μ m	8	16	68	273	68	68
Charge density, g/cm ³	1.583	1.614	1.616	1.604	1.621	0.886
Percent of TNT	4.9	95.2	95.2	94.7	94.7	52.2
Charge weight, g	3	23	23	23	23	13
-AN detonation ^h						
Experimental						
Calculated from products						
Products, mol/mol HE						
H ₂	105 + 11	1120 + 11	1106 + 11	1088 + 11	1023 + 10	1052 + 11
H ₂ O	162 ± 18	1123 ± 28	1080 ± 28	1068 ± 28	993 ± 32	1013 ± 22
CO ₂	.700	0.917	0.885	0.884	0.992	0.984
CO	.01	1.87	1.84	1.88	2.23	1.40
C(s)	.626	0.581	0.583	0.558	0.463	0.585
H ₂	.580	0.091	0.139	0.122	0.029	0.617
NH ₃	.26	0.596	0.464	0.540	0.090	0
CH ₄	.161	0.018	0.026	0.024	i	0.317
HCN	.070	0.0008	0.033	0.013	i	0.054
H ₂ O	.0029	0.0025	0.0026	0.0012	i	0.0048
NO	.0069	0.0002	0.0020	0.0016	i	0.0028
NO ₂	trace	0.029	0.022	0.015	0.101	i
	.0031	0.032	0.120	0.151	0.214	i
		0.0019	i	i	i	i
Material recovery, mol%						
C	3.5	53.7	61.6	57.6	85.7	101.5
H	3.1	98.7	98.0	98.9	99.6	92.4
N	5.3	96.1	86.4	96.7	99.3	100.8
O	3.6	96.8	99.0	99.1	98.9	99.1

^a C₂.475H₂.716N₁.553O₂.860 (MW = 1).

^b C₁.272H₃.843N₂.012O₃.291 (MW = 1), trace of C₂H₂ detected.

^c Approximately balanced to H₂O + .

^d C₁.191H₃.917N₂.043O₃.321 (MW = 1).

^e C₁.222H₃.888N₂.032O₃.309 (MW = 1).

^f 0.5-g PETN booster required in a titration to detonator.

^g C₀.582H₄.469N₂.276O₃.539 (MW = 1), approximately balanced to H₂O + CO₂.

^h 298 K, H₂O(l) (cal/g).

ⁱ Not detected.

Table 2. Heats and products of detonation of amatol 20/80 using $^{14}\text{NH}_4^{14}\text{NO}_3$ and $^{15}\text{NH}_4^{15}\text{NO}_3$ in a uniform mixture.

Experimental conditions	Type of AN	
	A^{14}N	A^{15}N
Composition (AN/TNT), wt%	19.7/80.3 ^a	20/80 ^b
AN particle size (W/50), μm	68	28
Charge density, g/cm^3	1.583	1.589
Percent of TMD	94.9	95.3
Charge weight, g	23	23
$-\Delta H$ detonation ^c		
Experimental	1105 $\pm$ 11	1112 $\pm$ 11
calculated from products	1062 $\pm$ 18	1031 $\pm$ 20
Products, mol/mol HE		
N_2 (^{14}N - ^{14}N)	0.700	0.410
N_2 (^{15}N - ^{15}N)	-	0.199
N_2 (^{14}N - ^{15}N)	-	0.0506
H_2O	1.01	1.01
CO_2	0.626	0.606
CO	0.580	0.580
C(s)	1.26	1.24
H_2	0.161	0.134
NH_3	0.070	0.080
CH_4	0.0029	0.027
HCN	0.0069	0.011
^{14}NO	0.0031	0.0088
^{15}NO	-	0.0051
$^{14}\text{N}^{14}\text{NO}$	Trace	0.0082
$^{15}\text{N}^{15}\text{NO}$	-	0.0029
$^{14}\text{N}^{15}\text{NO}$	-	0.0016
C_2H_2	Not observed	0.0008
CH_2O	Not observed	Trace
Material recovery, mol%		
C	50.5	50.0
H	95.1	96.4
^{14}N	95.3	83.4
^{15}N	-	94.3
O	99.6	99.3

^a $\text{C}_{2.457}\text{H}_{2.716}\text{N}_{1.553}\text{O}_{2.860}$ (MW = 100).

^b $\text{C}_{2.465}\text{H}_{2.718}\text{N}_{1.057}^{15}\text{O}_{2.844}$ (MW = 100).

^c 298 K, $\text{H}_2\text{O}(\text{l})$ (cal/g).

Table 3. Isotopic labeling in uniformly mixed 20/80 amatol and the nitrogenous detonation product.

Conditions ^a	$^{15}\text{N}^{15}\text{N}$, mol	$^{14}\text{N}^{15}\text{N}$, mol	$^{14}\text{N}^{14}\text{N}$, mol
Expected for 100% mixing	0.051	0.384	0.336
Expected for 0% mixing	0.244	--	0.529
Experimental results	0.199	0.051	0.410

^a Initial labeling of TNT and $^{15}\text{NH}_4^{15}\text{NO}_5$: 1.057 g-atoms ^{14}N per mol HE and 0.488 g-atoms ^{15}N per mol HE.

more carbon, this energy gain is nearly offset by the endothermic formation of greater quantities of nitrogen oxides.

Comparing columns 3 and 6 shows the effect of reducing the charge density while holding all other parameters constant. Detonation temperatures increase, pressures decrease, and product composition changes: those product species (CO and H_2) representative of a higher-temperature but lower-pressure process increase and those species (CO_2 , H_2O , and C(s)) representative of a lower-temperature, higher-pressure process correspondingly decrease. There is also a corresponding small decrease in the heat of detonation.

Table 2 gives the results of an experiment with the uniformly distributed ^{15}N . This formulation contained 1.057 g-atoms of ^{14}N and 0.488 g-atoms of ^{15}N per mol of amatol. Table 3 gives the isotopic distribution of the nitrogen gas from which we calculate that about 13% of the nitrogen in the TNT and AN detonation products mixed $[(0.051)/(0.384) \times 100]$.

Table 4 gives the results of the annulus experiment in which the core of the charge contained ^{15}N . This formulation contained 1.430 g-atoms of ^{14}N and 0.124 g-atoms of ^{15}N per mol of amatol. Table 5 gives the isotopic distribution of the nitrogen gas from which we calculate that about 12% of the nitrogen in the TNT and AN detonation products mixed $[(0.062 - 0.057)/(0.062 - 0.0196) \times 100]$. Because the mixing in the two experiments was the same, we concluded that the rate of mixing was constant across the diameter of the charge.

Table 4. Heats and products of detonation of TNT/A¹⁴N and TNT/A¹⁵N (80/20)^a in the annulus experiment.

	Charge configuration	
	Annulus	Core
Explosive	TNT/ ¹⁴ NH ₄ ¹⁴ NO ₃	TNT/ ¹⁵ NH ₄ ¹⁵ NO ₃
Charge dimensions, mm		
Inside diameter	6.35	
Outside diameter	12.7	6.35
Length	114	114
Charge density, g/cm ³	1.584	1.585
Percent of TMD	95.0	95.0
Charge weight, g	17.22	5.88
-ΔH detonation ^b		
Experimental	1117 ± 11	
Calculated from products	955 ± 150	
Products, mol/mol HE		
	¹⁴ N ¹⁴ N	0.628
	¹⁵ N ¹⁵ N	0.057
	¹⁴ N ¹⁵ N	0.015
	H ₂ O	1.02
	CO ₂	0.500
	CO	0.545
	C(s)	1.23
	H ₂	0.151
	NH ₃	0.073
	CH ₄	0.0027
	HCN	0.0026
	¹⁵ NO	0.0040
	¹⁵ N ¹⁵ NO	0.0028
	¹⁴ N ¹⁵ NO	0.0017
	C ₂ H ₂	0.0003
	CH ₂ O	0.0040
Material recovery, mol%		
	C	50.4
	H	97.7
	¹⁴ N	94.3
	¹⁵ N	116
	O	99.0

^a Composition by formulation; the empirical formula is
 $C_{2.465}H_{2.754}^{14}N_{1.430}^{14}N_{0.124}^{15}O_{2.858}$ (MW = 100).

^b 298 K, H₂O(l) (cal/g).

Table 5. Isotopic labeling of the nitrogenous detonation products produced in the annulus-containing 20/80 amatol experiment.

Conditions ^a	¹⁵ N ¹⁵ N, mol	¹⁴ N ¹⁵ N, mol	¹⁴ N ¹⁴ N, mol
Expected for 100% mixing	0.0196	0.0848	0.673
Expected for 0% mixing	0.062	—	0.715
Experimental results	0.057	0.015	0.628

^a Initial labeling of TNT, ¹⁴NH₄¹⁴NO₃, and ¹⁵NH₄¹⁵NO₃: 1.430 g-atoms ¹⁴N and 0.124 g-atoms ¹⁵N per mol of HE.

1-Ammonium-3,5-dinitro-1,2,4-triazole (ADNT) and
Ammonium Nitrate (AN)/ADNT

Rationale. ADNT and AN/ADNT were studied at the request of Los Alamos National Laboratory (LANL) as part of a nonideal explosives research study involving AN. The explosive of principal interest was AN/ADNT. ADNT was studied to better understand the behavior of the mixture.

Experimental. ADNT (C₂H₄N₆O₄, MW = 176.1) has a mp of 168°C and is stoichiometrically balanced to H₂O and CO. AN/ADNT at a mol ratio of 2:1 (47.6/52.4 wt%) is balanced to H₂O and CO₂. The mp of the mixture is 112°C.¹⁵ The compositional analysis of the material used was 47.2/52.8 wt%, from which we calculated an empirical formula of C_{0.666}H_{3.59}N_{2.98}O_{2.97} (MW = 100).

Both materials were prepared at LANL¹⁶ and were used as received after storage under vacuum in a desiccator. A 0.5-g PETN booster was used in addition to the standard detonator.

Results and Discussion. Table 6 contains the results obtained for both explosives. ADNT gave a ΔH detonation of 1135 cal/g, which agreed well with the computer-calculated value of 1173 cal/g at 1726 K. As expected for a CO-balanced explosive, considerable amounts of CO and solid carbon and some H₂ were produced in addition to much N₂, H₂O, and CO₂. As is usual

Table 6. Heats and products of detonation of ADNT^a and AN/ADNT.^b

Experimental conditions		Explosive	
		ADNT, detonation	AN/ADNT, detonation
Charge density, g/cm ³		1.574	1.639
Percent of TMD		96.4	97.9
Charge weight, g		22.9	23.6
-ΔH detonation ^c			
Experimental		1135 ± 11	1213 ± 12
Calculated from products		1251 ± 87 ^d	1263 ± 40
Products, mol/mol HE	N ₂	2.92	1.47
	H ₂ O	1.53	1.78
	CO ₂	1.03	0.592
	CO	0.658	0.0092
	C(s)	0.271	0
	H ₂	0.133	0.0096
	NH ₃	0.010	0.0006
	CH ₄	0.029	Not detected
	HCN	0.018	0.0005
	NO	Not detected	0.0013
Material recovery, mol%	C	87.0	100
	H	93.5	101
	N	97.7	99
	O	106	100

^a ADNT = ammonium dinitrotriazole, C₂H₄N₆O₄ (MW = 176.1); a purity analysis was not conducted.

^b AN/ADNT (2:1 mol ratio), 47.2/52.8 wt% by analysis; C_{0.666}H_{3.558}N_{2.979}O_{2.968} (MW = 100).

^c 298 K, H₂O(l) (cal/g).

^d These errors are large because of the large uncertainty in the ΔH_f[°] for ADNT (+0.6 ± 2.0 kcal/mol).

for explosives that produce solid carbon, the material recovery had deteriorated somewhat. The ΔH detonation calculated from the products did not agree well with the experimental value—even though the assigned error limit was large. The major contributor to the large error limit was the uncertainty in the ΔH_f[°] of ADNT (+0.6 ± 2.0 kcal/mol). Poor material recovery was also a factor in the lack of agreement between the experimental ΔH detonation and that calculated from the products.

AN/ADNT gave a ΔH detonation that agreed reasonably well with the computer-calculated value of 1260 cal/g at 1665 K and agreed, within assigned error limits, with the value calculated from the products. AN/ADNT gave essentially only N_2 , H_2O , and CO_2 , as we would expect from a CO_2 -balanced explosive. The material balance for AN/ADNT was excellent.

It is noteworthy that the addition of AN to bring ADNT from CO to CO_2 balance resulted in a very modest increase in ΔH detonation. Because of the nature of the products from AN/ADNT and their agreement with calculated values, it is clear that heavily confined AN/ADNT behaves ideally (i.e., the components interact completely as a homogeneous explosive) at a density of 1.64 g/cm³ and a diameter of 12.7 mm.

Benzotrifuroxan (BTF)

Rationale. BTF was studied primarily because it contains no hydrogen. It was part of a carefully selected series of explosives of differing elemental composition. BTF has a high detonation temperature and, if pure, cannot produce water or hydrogen. Reference 3 gives further details.

Experimental. BTF¹⁷ ($C_6N_6O_6$) was purchased and used as received. The mp was 196.3–197.0°C. Elemental analyses for carbon and nitrogen agreed with theory for $C_6N_6O_6$. Hydrogen content, on the basis of product recovery from these experiments, was 0.07–0.09 wt%—below the limit for reliable hydrogen analysis. Chlorine was detected (0.3 wt%); it could have come from trichlorobenzene, the starting material, or trichlorotrinitrobenzene (a synthetic intermediate), but neither of these materials nor triazidotrinitrobenzene (another intermediate) was detected by thin-layer chromatography (TLC). TLC analysis did show unidentified impurities that did not appear to be nitro or nitroso compounds when tested colorimetrically. Small amounts of these impurities are most probably present in the trichlorobenzene and are retained through the entire synthesis. On the basis of the above work and IR spectral analysis, the purity of the BTF was conservatively estimated to exceed 95%.

Because an exploding bridgewire can initiate BTF, the detonators for this study contained only BTF, a 0.15-g high-density pellet next to the main charge, and about 0.10 g of powder packed around the bridgewire.

Results and Discussion. Table 7 lists the results of work with both heavily confined and unconfined BTF charges. One experiment resulted in an unintentional deflagration, and these results are combined with those from unconfined detonation. Products from unconfined detonations and deflagrations are comparable because, inside the calorimeter bomb, they both equilibrate under conditions of high temperature and low pressure relative to the CJ isentrope. Results from these two kinds of experiments were averaged and presented in the right-hand column. Error limits show the excellent agreement between these two experiments. This explosive, with little hydrogen present,

Table 7. The heat and products of detonation and deflagration of BTF.^a

Experimental conditions		Detonation	Deflagration and unconfined detonation
Charge density, g/cm ³		1.86	1.84
Charge wt, g		22	14 and 23 ^b
Number of experiments		2	2
-ΔH reaction ^c			
Experimental		1411 ± 11	1166 ± 9
Calculated from products		1475 ± 18	1215 ± 15
Products, mol/mol HE	N ₂	2.93	2.98
	H ₂ O	0.09	0.030
	CO ₂	1.56	0.006
	CO	2.87	6.03
	C(s)	1.57	Not detected
	H ₂	0.010	0.039
	NH ₃	0.005	0.002
	HCN	0.005	0.007
Material recovery, mol%	C	73.9	100.6
	H ^d	111	90.1
	N	98.4	100.0
	O	100.5	100.9
	Cl ^e	0	0

^a BTF = C_{6.00}H_{0.20}N_{5.96}Cl_{0.021} by analysis and adjusted to C = 6 (MW = 156.5).

^b 0.5-in-diam and 1.0-in-diam charges.

^c 298 K, H₂O(l) (cal/g).

^d Hydrogen content of explosive is uncertain. Best value is based on recovery from these experiments.

^e No products containing chlorine were detected.

also shows the effects of pressure and temperature on product composition. The right column shows a dramatic increase in CO and decreases in CO₂ and C(s).

1,2-Bis(difluoroamino) Perfluorocyclobutane (BDFPCB)/
Tris(difluoroamino) Perfluorobutane (TDFPB)

Rationale. This mixture (BDFPCB/TDFPB; 92.8/7.2 wt%) was studied as part of a fluorine-oxidizer study funded by the Office of Naval Research.

Experimental. BDFPCB and TDFPB, both liquids, were purchased¹⁸ and mixed because we did not have enough of either material to conduct the desired tests. (This was the first time that either material had been synthesized.) The empirical formula for the mixture was C_{1.481}N_{0.761}O_{3.766} (MW = 100). BDFPCB (C₄N₂F₁₀) has a bp of 58-59°C and a density of 1.63 g/cm³. TDFPB (C₄N₃F₁₃) has a bp of 58-60°C at 300 mm Hg and a density of 1.77 g/cm³. They were fired in the liquid configuration described in the experimental section, and the Monel bomb was used. A 0.7-g PETN booster was used in addition to the detonator.

Results and Discussion. Results are presented in Table 8. Although the experiment was not a detonation, the materials were so highly over-balanced in the oxidizer fluorine that, from our experience, we expected no difference in the products resulting from detonation and deflagration. The results given were corrected for PETN present in the initiation system and for its reaction with fluorine to produce HF and with free carbon to produce both CO and traces of CO₂. As predicted by computer calculations, all of the fluorine appears as CF₄ in the products.

BDFPCB-TDFPB/Al

Rationale. BDFPCB-TDFPB/Al was studied as part of a fluorine oxidizer program funded by the Office of Naval Research in which we compared the effects of the detonation products Al₂O₃ and AlF₃ on explosive performance.

Table 8. Heat and products of detonation of BDFPCB/TDFPB.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.64
Charge weight, g		21
-ΔH detonation ^b		
Experimental		997 ± 20
Calculated from products		888 ± 50
Products, mol/mol HE	N ₂	0.382
	C(s)	0.416
	CF ₄ ^c	0.887
	C ₂ N ₂	0.004
Material recovery, mol%	C	60.5
	N	102
	F	100

^a BDFPCB = 1,2-bis(difluoroamino) perfluorocyclobutane, C₄N₂F₁₀; TDFPB = tris(difluoroamino) perfluorobutane, C₄N₃F₁₃ (92/7.2 wt% mixture), C_{1.481}N_{0.761}F_{3.766} (MW = 100). Corrected for PETN in the initiation system and its reaction with fluorine to produce HF and with free carbon to produce mostly CO.

^b 298 K, H₂O(l) (cal/g).

^c Based on total fluorine contained in system.

Experimental. Our intent was to balance the BDFPCB-TDFPB/Al mixture to AlF₃ and solid carbon. However, analysis of the starting aluminum (Alcoa 1660 flake; particle size range: 3-65 μm) showed it was only 86.5 wt% active aluminum, the balance being 10.11 wt% Al₂O₃, 2.77 wt% stearic acid (C₁₈H₃₆O₂), and 0.63 wt% H₂O. Other performance experiments had already been made assuming that Alcoa 1660 (a grade of aluminum flakes produced for the explosives industry) was 100% active aluminum, and we wanted to fire the same composition as had been previously used. This composition was actually over-balanced with respect to AlF₃ and solid carbon. In addition, after several months, BDFPCB (the more volatile component of the mixture) had decreased so that the composition was 79.6/20.4 wt%. To keep the aluminum in suspension as a stable gel, we added 0.75 wt% Cab-O-Sil (SiO₂).

The final composition we fired was BDFPCB (59.02%)/TDFPB (15.12%)/Al (20.74%)/Al₂O₃ (2.68%)/H₂O (0.017%)/C₁₈H₃₆O₂ (0.70%)/SiO₂ (0.75%). For

this composition, we calculated the empirical formula $C_{1.111}H_{0.0897}N_{0.578}O_{0.110}F_{2.802}Al_{0.858}Si_{0.0125}$ (MW = 100).

We used the configuration for liquids described in the experimental section and the Monel bomb. Because there was a limited amount of NF_2 explosive, it was necessary to reduce the charge diameter to 6.35 mm. The BDFPCB-TDFPB/Al mixture proved to be very impact-sensitive. To protect the operator, the operations of mixing, loading the shot cylinder, and sealing the cylinder and calorimeter bomb were conducted remotely.

Results and Discussion. Results are given in Table 9. The most abundant gas was CO, which was quite unexpected from an explosive containing limited oxygen sources (PETN, stearic acid, SiO_2 , and H_2O). Also, far too much HF was produced from the known limited sources of hydrogen. On the basis of the material balances, large amounts of hydrogen and oxygen clearly came from a source as yet unidentified. We noted that the molar ratio of hydrogen and oxygen was approximately that for water. SiF_4 must have resulted from the reaction of HF with SiO_2 . The only product detected containing aluminum was AlF_3 , but the aluminum recovery was less than 100%. We therefore assumed that all of the aluminum was converted to AlF_3 , and we adjusted the AlF_3 value to minimize aluminum and fluorine recovery errors.

1,2-Bis(difluoroamino) Propane (1,2-DP)

Rationale. 1,2-DP was studied primarily because fluorine replaces oxygen as the oxidizer, and it was of critical interest to determine if CF_4 was a product. Computer calculations indicated that only very small amounts of CF_4 would be present at the freeze-out temperature. Reference 3 gives further details.

Experimental. 1,2-DP, a liquid (bp $78^\circ C$), was furnished¹⁹ as a 20% solution in dichloromethane, which was removed by fractionating through a distillation column at 0.5 atm. The empirical formula based on elemental analysis and adjusted to C = 3 is $C_{3.00}H_{6.02}N_{2.02}F_{3.58}$ (MW = 138.4). We were unable to establish the purity by gas-liquid chromatography (GLC).

Because of the suspected high shock sensitivity of 1,2-DP, it was necessary that certain operations--distilling the solvent, loading and sealing the gold shot cylinder, and closing of the calorimeter bomb--be conducted

Table 9. Heat and products of detonation of BDFPCB-TDFPB/Al.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.76
Percent of TMD		96
Charge weight, g		8.9
Charge diameter, mm		6.35
-ΔH detonation ^b		
Experimental		2257 ± 25
Calculated from products		2445 ± 150
Products, mol/mol HE	N ₂	0.28
	H ₂ O	0.056
	CO	0.30
	C(s)	0.84
	H ₂	0.039
	CH ₄	0.0002
	HCN	0.0025
	HF	0.46
	AlF ₃ ^c	0.82
	SiF ₄	0.0083
Material recovery, mol%	C	27.6
	H	436
	N	96.2
	O	181
	F	105
	Al	95.0
	Si	64.0

^a BDFPCB-TDFPB/Al (74.7/25.3 wt%). BDFPCB = 1,2-bis(difluoroamino) perfluorocyclobutane, C₄N₂F₁₀; TDFPB = tris(difluoroamino) perfluorobutane, (79.6/20.4 wt% mixture), C_{1.111}H_{0.0897}N_{0.578}O_{0.110}F_{2.802}Al_{0.858}Si_{0.0125}, by analysis and calculation. 0.75 wt% of Cabosil was added for stabilization.

^b 298 K, H₂O(l) (cal/g).

^c We assumed that all aluminum reacts to form AlF₃ and adjusted the AlF₃ value so that aluminum and fluorine recovery were equally close to 100%.

remotely. However, it proved necessary to use a 0.75-g PETN booster in addition to the standard detonator. We used the configuration for liquids described in the experimental section, the Monel bomb, and the special water and HF traps containing potassium fluoride.

Results and Discussion. Table 10 lists the results of the 1,2-DP work. One experiment resulted in an unintentional deflagration and these results are also presented. All results are corrected as indicated in footnote b of Table 10.

Table 10. Heat and products of detonation and deflagration of 1,2-bis(difluoroamino) propane.^{a,b}

Experimental conditions		Detonation	Deflagration
Charge density, g/cm ³		1.265	1.265
Charge weight, g		18	18
Number of experiments		2	1
-ΔH reaction ^c			
Experimental		1339 + 35	1320
Calculated from products		1415 + 40	1399
Products, ^d mol/mol 1,2-DP			
	N ₂	1.11	1.05
	C(s)	2.88	3.00
	H ₂	0.29	0.77
	NH ₃	0.031	0.030
	CH ₄	0.13	0.0083
	HF(g) ^e	4.00	4.00
	C ₂ H ₆	0.002	Not detected
	C ₂ H ₄	0.009	Not detected
Material recovery, mol%			
	C	11.9 + 1.0	12.5
	H	87.7 + 4.6	94.2
	N	112.6 + 5.4	106.0
	F ^f	78.6 + 4.0	78.6

^a 1,2-DP = C_{3.00}H_{6.02}N_{2.02}F_{3.58} by analysis and adjusted to C = 3 (MW = 138.4).

^b Results are corrected for reaction of PETN products with C(s), for reaction of HF with Monel, and for reaction of HF with NH₃.

^c 298 K, HF(g) (cal/g).

^d CF₄ was considered as a possible product but was not detected.

^e Based on total fluorine contained in 1,2-DP.

^f Observed, not corrected, values used in calculation.

The most significant result is that CF₄, a stable, easily identified gas, was not observed. Only HF was observed, which provided a qualitative confirmation of the calculations. Products from deflagrations equilibrate under conditions of high temperature and low pressure relative to those on the CJ isentrope. Hydrogen is the only major product that shows a significant change. Heats of reaction are essentially unchanged between detonation and deflagration. Material balances are much poorer than usual. The differences between the corrected experimental ΔH_{reaction} and that calculated from the corrected products were also much greater than usual. These differences were most likely caused by our inability to establish the purity of 1,2-DP and failure to identify and correct for all the side reactions that occurred.

Bis(2,2-dinitro-2-fluoroethyl) Formal (FEFO)

Rationale. FEFO was studied primarily because it contains both oxygen and fluorine as oxidizers. It was another of a carefully selected series of explosives of differing elemental composition. It was also of interest to determine if CF_4 was a product; computer calculations indicated it would not be. Reference 2 gives further details.

Experimental. FEFO was available at the time in only research quantities. It is a nonvolatile liquid having a vapor pressure of about 40 μm at 90°C. The sample was determined to be 97.4% pure by GLC analysis. The principal impurity was bis(2,2-dinitro-2-fluoroethyl) diformal. The empirical formula based on elemental analysis and adjusted to C = 5 was $\text{C}_{5.00}\text{H}_{5.738}\text{N}_{4.089}\text{O}_{10.057}\text{F}_{1.866}$ (MW = 319.5). The sample we tested contained 0.1% water, which was removed by vacuum distillation. To initiate the charge, a 0.3-g PETN booster was required in addition to the standard detonator.

These experiments were conducted before a Monel bomb was available. About 65% of the fluorine in FEFO was recovered as HF and about 23% as metal fluorides in solution. Because no other products containing fluorine could be detected, we concluded that all of the fluorine must appear as HF in the detonation products and that the fluorine not observed as HF had reacted with the stainless steel bomb. The observed heats of reaction and products were corrected for these reactions.

Results and Discussion. Results are listed in Table 11 with those from one experiment that resulted in an unintentional deflagration. All of the fluorine appears as HF and no CF_4 was detected, again providing a qualitative confirmation of the calculations.

The differences in products and energy usually observed between the high-temperature, low-pressure equilibration of a deflagration and lower-temperature, higher-pressure equilibration of a detonation are not evident with FEFO. The two columns of data are essentially identical. The reason is that FEFO is very nearly oxidizer-balanced to HF, H_2O , and CO_2 . For materials that are CO_2 balanced, there are no differences in heat and products between heavily confined, unconfined, and deflagration experiments.

Table 11. Heat and products of detonation and deflagration of Bis(2,2-dinitro-2-fluoroethyl) formal (FEFO).^a

Experimental conditions		Detonation	Deflagration
Charge density, g/cm ³		1.60	1.60
Charge weight, g		25	25
Number of experiments		2	1
-ΔH reaction ^b			
Experimental		1279 ± 13	1293
Calculated from products		1364 ± 32	1363
Products, mol/mol FEFO	N ₂	1.99	1.99
	H ₂ O	2.14	2.16
	CO ₂	3.16	3.15
	CO	1.88	1.90
	H ₂	0.046	0.037
	NH ₃	0.023	0.021
	CH ₄	0.0009	Trace
	HF ^c	1.87	1.87
Material recovery, mol%	C	101	101
	H	110	110
	N	97.7	97.7
	O	103	103
	F ^d	89.2	84.6

^a FEFO = C_{5.000}H_{5.738}N_{4.089}O_{10.057}F_{1.866} by analysis and adjusted to C = 5 (MW = 319.5). Results corrected for HF reaction with stainless steel.

^b 298 K, HF(g), H₂O(l) (cal/g).

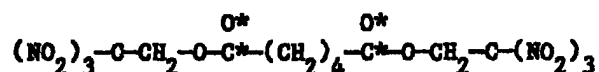
^c Calculated from total fluorine contained in FEFO.

^d Observed values used in calculation.

Bis(trinitroethyl) Adipate (BTNEA)

Rationale. The CJ theory of detonation usually envisions a rapid reaction in which a rather complex organic molecule is converted to a mixture of simple gaseous product molecules. Whether this process occurs 1) by an almost simultaneous breaking of all bonds of the reactant molecule followed by random recombination of atoms to form the product molecules or 2) by a process that retains some structural features of the reactant molecule is a question that, to our knowledge, has not been addressed experimentally. Our study used an isotopically labeled explosive to distinguish between the two mechanisms. Reference 4 gives further details.

Experimental. The explosive molecule designed for the experiment was BTNEA ($\underline{1}$, $C_{10}H_{12}N_6O_{16}$, MW = 472.3). This compound was chosen because its structure contains essentially preformed molecules of CO and/or CO_2 . The BTNEA was synthesized²⁰ with isotopic labels (^{13}C and ^{18}O) in the ester carbonyl moieties at the positions indicated by asterisks.



1

Table 12. Heat and products of detonation of bis(trinitroethyl) adipate.^a

Experimental conditions	Unlabeled, detonation	Unlabeled, detonation	Labeled, detonation
Charge density, g/cm ³	1.59	1.54	1.57
Charge diameter, mm	12.7	6.35	6.35
Charge weight, g	23	5	3.9
Number of experiments	2	2	1
-ΔH reaction^b			
Experimental	1148 ± 11	Not determined	Not determined
Calculated from products	1170 ± 20	1171 ± 20	1169
Products, mol/mol BTNEA			
N ₂	2.70	2.69	2.59
H ₂ O	4.25	4.32	4.41
CO ₂	4.07	3.94	3.80 ^c
CO	3.58	3.88	3.67 ^c
C(s)	2.16	2.00	2.37 ^c
H ₂	0.73	0.79	0.72
NH ₃	0.37	0.29	0.22
CH ₄	0.13	0.12	0.11
HCN	0.06	0.06	0.053
Material recovery, mol%			
C	78.5	80.6	77.3
H	97.2	97.0	95.4
N	97.1	95.6	91.2
O	99.9	101	98.1

^a Cylindrical charges confined in gold cylinders of wall thickness equal to the charge diameter. BTNEA = $C_{10}H_{12}N_6O_{16}$ (MW = 472.3).

^b 298 K, H₂O(l) (cal/g).

^c Because of complications resulting from separation of gases to facilitate isotopic analysis, these values are not deemed as accurate as those on the unlabeled material.

Table 13. Isotopic ratios in BTNEA and its detonation products.

	Isotopic ratio	
	$^{12}\text{C}/^{13}\text{C}$	$^{16}\text{O}/^{18}\text{O}$
<u>Starting material</u>		
Labeled BTNEA ^a	4.80	11.70
<u>Products</u>		
H ₂ O	-	16.57 ^b
CO ₂	4.69	11.40
CO	4.78	11.19
C(s)	4.60	-
CH ₄	4.33	-

^a Isotopic ratios are based on calculated isotopic purity.

^b This high value resulted from a delay in the analysis of the sample during which time it partially equilibrated with atmospheric oxygen.

Results and Discussion. Results are presented in Tables 12 and 13. The ratios of $^{12}\text{C}/^{13}\text{C}$ and of $^{16}\text{O}/^{18}\text{O}$ are essentially the same for all of the product species and are equal to the isotopic ratios in the initial BTNEA. This statistical scrambling of the isotopic labels into all of the C- or O-containing product species is consistent with extensive atomic diffusion and randomization of atoms. If all or, at least, a high percentage of the ^{13}C and ^{18}O had appeared in the CO and CO₂ products, the experiment would have indicated that some structural features of the reactant are retained and that atomic diffusion is minimized, suggesting that an easy mechanism to stable products. Such retention was not observed. The ratio of $^{12}\text{C}/^{13}\text{C}$ in the solid carbon and methane is especially significant. If there were only 10% retention, these isotope ratios would be about 5.5. The difference is greater the experimental error of the determination and would have been easily detected.

We conclude that, in the case of a homogeneous ideal explosive, all of the bonds of the original explosive molecule are broken during the detonation process. These molecular fragments must then recombine in a statistically random fashion before the kinetic "freeze out" of products during the adiabatic expansion.

Bitetrazole (BTZ)

Rationale. BTZ is an oxygen-free explosive having a large positive heat of formation. It was one of a carefully selected series of explosives of differing elemental composition intended for a variety of basic research studies. Product composition data were of particular interest.

Experimental. BTZ ($C_2H_2N_8$), Grade A, was purchased²¹ wet with hexane and dried before use. The composition was determined by elemental analysis; we calculated an empirical formula, adjusting C = 2, of $C_{2.000}H_{1.939}N_{7.704}$ (MW = 133.9). The particle size, 50% wt average, was 15-20 μm . The TMD is 1.685 g/cm³. The maximum density to which the material was pressed was 1.577 g/cm³, 94% TMD.

Results and Discussion. Results are presented in Table 14. The hydrogen and nitrogen material recoveries were considerably poorer than usual. This fact,

Table 14. Heat and products of detonation of bitetrazole.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.577
Charge weight, g		23
Number of experiments		1
-ΔH reaction^b		
Experimental		823 ± 16
Calculated from products		996 ± 160
Products, mol/mol HE	N ₂	3.37
	C(s)	1.90
	H ₂	0.065
	NH ₃	0.41
	CH ₄	0.035
	HCN	0.054
	C ₂ H ₂	0.0004
Material recovery, mol%	C	6.3
	H	85.4
	N	93.5

^a BTZ = $C_{2.000}H_{1.939}N_{7.704}$ by analysis and adjusted to C = 2 (MW = 133.9).

^b 298 K, H₂O(l) (cal/g).

combined with the uncertainties in ΔH_f° for solid carbon and bitetrazole, were the probable reasons for the large discrepancy between the observed and calculated ΔH detonation. For this reason, a rather high error range was assigned to the ΔH calculated from the products. Elemental analysis of the solid residue showed H: 1 and N: 13 wt%. This accounts for all of the missing nitrogen, but, as mentioned in the product analysis section, the form of this hydrogen and nitrogen in the solid residue has not been determined.

Bitetrazole with Hydrazine Nitrate and Bitetrazole with Benzotrifuroxan

Rationale. We investigated diffusion and equilibration processes in mixtures of ideal explosives using two chemical systems: bitetrazole (BTZ) with hydrazine nitrate (HN) and BTZ with benzotrifuroxan (BTF). In the BTZ/HN system, neither explosive can produce carbon oxides on its own whereas in the BTZ/BTF system, neither can produce water on its own. Depending on the experimental conditions used, the amounts of carbon oxides and water formed can provide information on the extent of diffusion and late-time vs early-time equilibration.

Experimental. We used bitetrazole (BTZ, $C_2H_2N_8$) with hydrazine nitrate (HN, $H_5N_3O_3$), 21.3/78.7 wt%, and BTZ with benzotrifuroxan (BTF, $C_6N_6O_6$), 50/50 wt%. Bitetrazole is described in Table 14. Hydrazine nitrate was stored wet with methanol and was purified by melting it under vacuum; this procedure reduced the methanol content to less than 0.01 wt%. The empirical formula based on elemental analysis and, adjusted to H = 5, is $H_{5.00}N_{2.85}O_{3.06}$ (MW = 94). The TMD is 1.665 g/cm^3 . The particle size, 50% weight average (W_{50}), was 15 μm .

Benzotrifuroxan was purified by recrystallization from benzene and dried at 60°C under vacuum. Benzene content was 0.17% by GLC. The empirical formula, on the basis of elemental analysis and adjusted to C = 6, is $C_{6.00}H_{0.39}N_{6.24}O_{5.49}$ (MW = 248). Particle size, W_{50} , was 4.5 μm .

The BTZ/HN system was balanced to CO at 21.3/78.7 wt% for which the empirical formula is $C_{0.318}H_{4.49}N_{3.61}O_{2.57}$ (MW = 100). The BTZ/BTF system was arbitrarily set at 50/50 wt% for which the empirical formula is $C_{1.96}H_{0.80}N_{4.14}O_{1.11}$ (MW = 100). The system was balanced well below the CO level that would be achieved if there were sufficient oxygen to combine with the remaining carbon.

Two experimental configurations were used for each system. The first was a physical mixture of the two explosives, which should result in maximum equilibration at early times. The second used two charges of pure explosive within the same cylinder separated by a 0.5-mm-thick gold diaphragm. In one BTZ/HN experiment, the gold diaphragm was purposefully omitted. In the latter configuration, BTZ was the lower charge in each system. This latter configuration should minimize early time equilibration and provide information on late-time, low-temperature equilibration.

Charges were pressed to about 95% TMD. BTZ/BTF mixtures were initiated with a 0.25-g BTF detonator. (The amount of BTF contained in the detonator was accounted for in the BTZ/BTF composition.)

Results and Discussion. Results for the BTZ/HN system are presented in Table 15. Simple calculations show that 45% of the carbon is converted to carbon oxides in the blended-powder experiment and only 8% is converted in the separated-charge experiments. The presence of the diaphragm made little difference in the total amount of carbon oxides produced.

Results for the BTZ/BTF system are given in Table 16. Simple calculations show that 45% of the hydrogen was converted to water in the blended-powder experiment and only 7% in the separated-charge experiments.

From these two systems, we conclude that, in mixtures of ideal explosives, diffusion plays an important role in the interaction of the two explosives and that there is very little, if any, late-time low-temperature equilibration.

Composition B (Comp B)

Rationale. Comp B was studied as part of an LLNL project to investigate the interaction between mixtures of ideal explosives.

Experimental. Comp B is RDX/TNT (63.79/36.21 wt% by analysis). The material was formulated by the author to be similar to Comp B, Grade A, but without any wax. Military grade RDX and TNT were used; the RDX was from the same lot as that used in the RDX study. The empirical formula is $C_{1.978}H_{2.520}N_{2.201}O_{2.679}$ (MW = 100).

Table 15. Heats and products of detonation of heavily confined mixed charges of bitetrazole/hydrazine nitrate.^a

Experimental conditions	Charge configuration		
	Blended powder, detonation	Separate charges with diaphragm, detonation	Separate charges without diaphragm, detonation
Charge density, g/cm ³	1.592	1.569/1.591	1.538/1.583
Percent of TMD	95.0	93.1/95.6	91.3/95.1
Charge weight, g	23	23	23
-ΔH detonation ^b			
Experimental	1286 ± 13	1154 ± 12	1179 ± 12
Calculated from products	1333 ± 30	1211 ± 30	1228 ± 30
Products, mol/mol HE			
N ₂	1.81	1.77	1.78
H ₂ O	2.15	2.13	2.17
CO ₂	0.133	0.0255	0.0113
CO	0.0103	0	0.0122
C(s)	0.172	0.277	0.274
H ₂	0.0216	0.0127	0.0186
NH ₃	0.0256	0.0123	0.0049
CH ₄	0.0024	0.0057	0.0084
HCN	0.0006	0.0007	0.0038
O ₂	0.0121	0.0628	0.0377
N ₂ O	Not observed	Not observed	0.0115
NO ₂	0.0030	0.0001	Trace
NO	0.0002	0.0033	Trace
HNO ₃	0.0020	0.0229	0.0169
C ₂ N ₂	Not observed	0.0054	0.0036
Material recovery, mol%			
C	49.2	18.4	18.8
H	98.7	97.3	99.1
N	101	99.4	100
O	96.1	92.9	91.8

^a BTZ/HN (21.3/78.7 wt%), C_{0.318}H_{4.49}N_{3.61}O_{2.57} (MW = 100), balanced to H₂O and CO.

^b 298 K, H₂O(l) (cal/g).

Results and Discussion. Results are presented in Table 17. The heat of detonation calculated from the products did not agree very well with the observed value. Hydrogen material recovery was quite good but that of nitrogen was not good. As expected, the heat of detonation and products of detonation of Comp B lie between the values for RDX and TNT when compared on an equal weight basis.

Table 16. Heat and products of detonation of heavily confined mixed charges of bitetrazole and benzotrifuroxan.^a

Experimental conditions	Charge configuration	
	Blended powder, detonation	Separate charges, detonation
Composition (BTF/BTZ), wt%	50.3/49.7	50.0/50.0
Charge density, g/cm ³	1.700	1.811/1.595
Percent of TMD	95.1	95.3/94.7
Charge weight, g	25	23
-ΔH detonation ^b		
Experimental	1128 ± 11	1121 ± 11
Calculated from products	1217 ± 75	1165 ± 35
Products, mol/mol HE		
N ₂	1.85	1.85
H ₂ O	0.077	0.012
CO ₂	0.25	0.17
CO	0.60	0.64
C(s)	1.07	1.06
H ₂	0.050	0.031
NH ₃	0.12	0.15
CH ₄	0.013	0.013
HCN	0.026	0.026
NO _x	0.0002	0.0004
C ₂ H ₆	0.0008	0.0005
Material recovery, mol%		
C	45.5	48.4
H	86.6	78.5
N	93.2	93.6
O	105	106.8

^a BTF/BTZ (50/50 wt%), C_{1.958}H_{0.803}N_{4.137}O_{1.108} (MW = 100).

^b 298 K, H₂O(l) (cal/g).

Cyclotetramethylene Tetranitramine (HMX)

Rationale. HMX was studied primarily because it is the principal ingredient of all DOE main-charge explosives. Also, it was one of a carefully selected series of explosives of differing elemental composition and density for which performance and product composition data as a function of charge density were of interest. Reference 2 gives further details.

Experimental. HMX is C₄H₈N₈O₈. The charges at densities 1.89 and 1.20 g/cm³ were Military Specification, Grade II HMX (mp 278-282°C).

Table 17. Heat and products of detonation of Composition B.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.74
Percent of TMD		99.0
Charge weight, g		25.1
-ΔH detonation ^b		
Experimental		1321 ± 13
Calculated from products		1249 ± 75
Products, mol/mol HE	N ₂	0.984
	H ₂ O	0.824
	CO ₂	0.597
	CO	0.609
	C(s)	0.728
	H ₂	0.167
	NH ₃	0.127
	CH ₄	0.029
	HCN	0.016
Material recovery, mol%	C	63.5
	H	99.1
	N	95.6
	O	98.0

^a Composition B = RDX/TNT (63.79/36.21 wt%). RDX contains 8.65% HMX.
The empirical formula is C_{1.978}H_{2.520}N_{2.201}O_{2.679} (MW = 100).

^b 298 K, H₂O(l) (cal/g).

Analysis by TLC showed about 0.5% cyclotrimethylene-trinitramine (RDX) and less than 1% each of an incompletely characterized linear nitramine (compound C) and 1-N-acetal-3,5,7-trinitrocyclotetranitramine. Charges were machined remotely from billets prepared using a special solvent-isostatic pressing technique.^{22,23}

For charges at density 0.73 g/cm³, specially prepared HMX of very low bulk density was used.²⁴ X-ray diffraction patterns showed the material to be β-HMX, and the purity estimated by TLC exceeded 99%. RDX was not detected by TLC. The moisture content after drying was 0.04%, and differential thermal analysis (DTA) produced a normal β-HMX thermogram. Charges were prepared by pressing 12.7-mm increments of the explosive directly into the shot cylinder. PETN boosters (0.3 g) were used for the confined experiments at density 1.89 and 1.20 g/cm³. No boosters were used for the other experiments.

Results and Discussion. Results from all experiments are presented in Table 18. For heavily confined charges (columns 1 through 3), the shift in products and energy is most dramatic between densities 1.89 and 1.20 g/cm³. Detonation temperatures increase and detonation pressures decrease with decreasing charge density. We observed that CO and H₂--product species representative of a high-temperature, low-pressure process--increased as density decreased and that CO₂, H₂O, and C(s)--species that are representative of a lower-temperature, higher-pressure process--correspondingly decreased.

Table 18. Heat and products of detonation of heavily confined HMX^a charges at three densities.

Experimental conditions		1 Confined, detonation	2 Confined, detonation	3 Confined, detonation	4 Unconfined, detonation
Charge density, g/cm ³		1.89	1.20	0.73 ± 0.04	1.89
Charge diameter, mm		12.7	12.7	12.7	25.4
Charge weight, g		25	18	11	24
Number of experiments		1	2	2	3
-ΔH reaction^b					
Experimental		1479 ± 12	1320 ± 18	1298 ± 3	1334 ± 9
Calculated from products		1514 ± 27	1351 ± 16	1331 ± 16	1334 ± 5
Products, mol/mol HMX	N ₂	3.68	3.91 ^c	4.00	4.02
	H ₂ O	3.18	2.77	2.70	2.50
	CO ₂	1.92	1.29	1.26	1.45
	CO	1.06	2.67	2.75	2.65
	C(s)	0.97	0	0	0
	H ₂	0.30	1.08	1.28	1.54
	NH ₃	0.39	0.107	0.011	Not detected
	CH ₄	0.039	0.011	Not detected	Not detected
	HCN	0.0081	0.0049	0.0015	0.0006
	C ₂ H ₆	0.001	Not detected	Not detected	Not detected
Material recovery, mol%	C	75.6	99.4	100	103
	H	104	101	99.9	101
	N	97.1	99.1	100	100
	O	101	100	99.5	101

^a HMX = C₄H₈N₈O₈ (MW = 296.17).

^b 298 K, H₂O(l) (cal/g). Confined charges are ΔH detonation.

^c The entire gas sample was lost from one experiment.

Unconfined charges were reshocked and equilibrated under conditions of high temperature and low pressure. Comparing columns 1 and 4 shows the corresponding effect of increased CO and H₂ and decreased CO₂, H₂O, and C(s).

Cyclotrimethylene Trinitramine (RDX)

Rationale. RDX was studied as part of an LLNL project to investigate the interaction between mixtures of ideal explosives.

Experimental. RDX (C₃H₆N₆O₆, MW = 222.1) has a mp of 205°C and is stoichiometrically balanced to H₂O and CO. Production material, Military Type B, Class A, was used. It was analyzed for HMX, and the composition was RDX/HMX (91.35/8.65 wt%). It was used as received after drying under vacuum in a desiccator.

Results and Discussion. Results are presented in Table 19. The heat of detonation calculated from the products agreed well with the observed value. As usual with explosives that produce solid carbon, material recoveries for hydrogen and nitrogen were low.

Ethylenediamine Dinitrate (EDN)

Rationale. EDN was studied as part of an investigation of nonideal explosives. The work was conducted under a research contract with the U.S. Air Force through Eglin Air Force Base. We planned to mix EDN with ammonium nitrate to study the interaction of the two materials.

Experimental. EDN (C₂H₁₀N₄O₆) was synthesized at LLNL following published procedures.²⁵ The mp determined by DTA was 186-187°C. A 0.5-g PETN booster was used with the standard detonator.

Results and Discussion. Results are presented in Table 20. Note the unusually large amount of water produced, probably a result of the large hydrogen content of EDN. Material recoveries were fair even though a considerable amount of carbon was formed.

Table 19. Heat and products of detonation of RDX.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.76
Percent of TMD		97.2
Charge weight, g		25.3
-ΔH detonation ^b		
Experimental		1452 ± 15
Calculated from products		1488 ± 20
Products, mol/mol RDX	N ₂	2.80
	H ₂ O	2.34
	CO ₂	1.39
	CO	1.10
	C(s)	0.44
	H ₂	0.34
	NH ₃	0.028
	CH ₄	0.041
Material recovery, mol%	HCN	0.029
	C	85.5
	H	94.0
	N	94.2
	O	104

^a RDX = Cyclotrimethylene trinitramine, C₃H₆N₆O₆ (MW = 222.1); RDX/HMX (91.35/8.65 wt% by analysis). Only the ΔH_f[°] changes because of HMX content; the empirical formula does not change.

^b 298 K, H₂O(l) (cal/g).

Ethylene Diamine Dinitrate/Ammonium Nitrate/RDX (EAR)

Rationale. EAR was studied as part of an investigation of nonideal explosives. The work was conducted under a research contract with the U.S. Air Force through Eglin Air Force Base. We were interested in the interaction of EA, a mixture of ethylene diamine dinitrate (EDN) and ammonium nitrate (AN). RDX was added so that the material would detonate reliably. The work with the unconfined charge of EAR was conducted primarily for seismic monitoring studies.

Experimental. EA is stoichiometrically balanced to CO₂ and H₂O at 44/56 wt%. At 49/51 wt%, it forms a binary eutectic mixture melting at 102°C. For experimental purposes, EA was formulated at 50/50 wt%.

Table 20. Heat and products of detonation of ethylenediamine dinitrate.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.524
Percent of TMD		95.5
Charge weight, g		22
-ΔH reaction ^b		
Experimental		1163 + 20
Calculated from products		1044 ± 100
Products, mol/mol HE	N ₂	1.40
	H ₂ O	3.05
	CO ₂	1.33
	CO	0.285
	C(s)	0.316
	H ₂	0.133
	NH ₃	1.02
	CH ₄	0.061
	HCN	0.0008
	NO	0.020
	NO ₂	0.020
	HNO ₃	0.0074
	C ₂ H ₆	0.0016
Material recovery, mol%	C	85.0
	H	96.7
	N	96.4
	O	101

^a EDN = C₂H₁₀N₄O₆.

^b 298 K, H₂O(l) (cal/g).

EAR was formulated as EDN/AN/RDX (42.5/42.5/15 wt%). The compositional analysis was 43.04/41.36/15.60 from which we calculated an empirical formula of C_{0.673}H_{4.800}N_{2.379}O_{3.358} (MW = 100). The oxygen balance of EAR to the H₂O-CO₂ level is -6.2%, which is higher than that for PETN (-10.1%). If EAR behaved ideally, we would expect little difference in product composition and energy between high- and low-density charges and between confined and unconfined charges, as we observed with PETN (Table 32). It was this possibility that generated an interest in EAR for seismic monitoring studies.

EAR was prepared at Eglin AFB²⁶ and used as received after drying under vacuum in a desiccator. For the charge at a density of 0.994 g/cm³, the material was ground in a ball mill to pass a 100-mesh sieve. We conducted witness plate tests using the unconfined configuration, and, comparing our results with TNT tests at the same density, we concluded that the EAR was sustaining detonation over the length of the 5.1-cm charge.

PETN boosters were required in addition to the standard detonator. We used a 0.5-g booster for the confined charge and a 2.5 g booster for the unconfined charge. Boosters were the same diameter as the charge.

Table 21. Heat and products of detonation of EAR.^a

Experimental conditions		Confined, detonation	Unconfined, reaction
Charge density, g/cm ³		1.593	0.994
Percent of TMD		94.9	59.2
Charge weight, g		23.1	25.1
Charge diameter, mm		12.7	25.4
-ΔH detonation ^b			
Experimental		1235 ± 12	1206 ± 12
Calculated from products		1263 ± 32	1198 ± 32
Products, mol/mol EAR	N ₂	1.13	1.19
	H ₂ O(l)	2.26	2.16
	CO ₂	0.539	0.512
	CO	0.067	0.160
	C(s)	0.053	c
	H ₂	0.041	0.237
	NH ₃	0.0091	c
	CH ₄	0.0040	c
	HCN	0.011	0.002
	NO	0.0007	c
Material recovery, mol%	C	92.7	99.8
	H	98.1	100
	N	95.7	100
	O	101.5	99.6

^a EAR = Ethylene diamine dinitrate/Ammonium nitrate/RDX (43.04/41.36/15.60 wt% by analysis), the empirical formula is C_{0.673}H_{4.800}N_{2.379}O_{3.358} (MW = 100).

^b 298 K, H₂O(l) (cal/g).

^c Not detected.

Results and Discussion. Table 21 gives the results. Confined EAR gave a ΔH detonation that agreed very well with the computer-calculated value of 1233 cal/g. The high H_2O and CO_2 values and low CO , $C(s)$, and H_2 values were consistent with those calculated for a high-oxygen-balanced explosive, and we concluded that heavily confined EAR at a density of 1.59 g/cm^3 and at 12.7 mm diameter behaves ideally.

Unconfined EAR at a density of 0.994 g/cm^3 gave a ΔH detonation that was slightly lower than that of the confined charge, but, considering the assigned error limits, the values were nearly the same. There were small increases in CO and H_2 and small decreases in H_2O , CO_2 , and $C(s)$. These changes were consistent with the slightly lower ΔH detonation value. We concluded that EAR at 1 in. diameter and at a density of 1.0 g/cm^3 is very close to ideal behavior and that for larger charges at this density it should behave ideally.

Ethylene Diamine Dinitrate/Ammonium Nitrate/RDX/Aluminum (EARL-1)

Rationale. EARL-1 was studied as part of an investigation of nonideal explosives. The work was conducted under a research contract with the U.S. Air Force through Eglin Air Force Base. We were interested in studying EA with RDX added to insure reliable detonation. A small amount of aluminum was added to increase the detonation temperature and to improve the interaction of EDN and AN.

Experimental. EARL-1 was formulated as EDN/AN/RDX/Al (40.3/40.3/14.2/5.2 wt%), which is stoichiometrically balanced to Al_2O_3 , H_2O , and CO . The compositional analysis was 41.1/40.9/11.9/6.2 wt% from which we calculated an empirical formula of $C_{0.602}H_{4.57}N_{2.23}O_{3.18}Al_{0.228}$ (MW = 100). The aluminum particle size was 1 to 5 μm .

EARL-1 was prepared at Eglin AFB²⁶ and used as received after drying under vacuum in a desiccator. In addition to the standard detonation, a 0.5-g PETN booster was required.

Results and Discussion. Table 22 gives the results for EARL-1. The experimental ΔH detonation of 1252 cal/g was considerably below the computer-calculated value of 1350 cal/g and the value of 1406 cal/g calculated from the observed products. An attempt to correct the experimental value for

Table 22. Heat and products of detonation of EARL-1.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.624
Percent of TMD		94.7
Charge weight, g		23.6
-ΔH detonation ^b		
Experimental		1252 ± 13
Calculated from products		1406 ± 32
Products, mol/mol EARL-1	N ₂	1.06
	H ₂ O(l)	2.07
	CO ₂	0.48
	CO	0.086
	C(s)	0.030
	H ₂	0.11
	NH ₃	0.0094
	CH ₄	0.0061
	HCN	0.0022
	Al	0.065
	Al ₂ O ₃	0.081
	NO	0.0009
	CH ₂ O	0.0002
Material recovery, mol%	C	95.5
	H	96.7
	N	96.0
	O	108
	Al	-

^a EARL-1 = EDD/AN/RDX/Al, 41.12/40.86/11.86/6.16 wt% by analysis; the empirical formula is C_{0.602}H_{4.571}N_{2.22}O_{3.18}Al_{0.228} (MW = 100).

^b 298 K, H₂O(l) (cal/g).

possible heat of hydration of Al₂O₃ increased even further the discrepancy between the experimental ΔH and the ΔH calculated from the observed products. Material recoveries based on the composition analysis were poorer than for EAR (Table 21), and this may partially account for the ΔH discrepancy. The high oxygen recovery was particularly surprising since oxygen recovery is usually best.

Of significant interest was the fact that 29 mol% of the aluminum was found unreacted in the solid residues from the experiment. Had all the aluminum reacted, the experimental ΔH would certainly have agreed more

closely with the computer-calculated value. This failure of aluminum to react completely in EARL-1 was verified by the results of cylinder tests. We concluded that EARL-1 was clearly not behaving ideally.

Hexanitrobenzene (HNB)

Rationale. HNB was studied because it was recently synthesized for the first time in the U.S., and it is the highest density, highest energy, CO₂-balanced organic explosive known to exist. As is true with BTF (Table 7), HNB has a high detonation temperature and, if pure, cannot produce water or hydrogen.

Experimental. HNB (C₆N₆O₁₂) was purchased¹⁸ and used as received. It is a yellow solid with a mp of about 240°C. The mp is difficult to determine because decomposition begins below this temperature. The material was held in a vacuum dessicator for about six months until we were able to study it. During this time it turned a reddish brown. IR analysis did not show impurities as compared to a sample of newly prepared material, which was considered to be the highest purity batch made. The exact purity is not known.

Because HNB is fairly sensitive, the detonator for this study contained a 0.20-g high-density HNB pellet next to the main charge and 0.085 g of PETN powder packed around the bridgewire.

Results and Discussion. Table 23 gives the results. The traps that held water and most of the ammonia blew their stopcocks on warming to room temperature. Thus, water could not be determined and only a lower limit value could be determined for ammonia. These products were not expected from the hydrogen-free HNB, but the fact that they could not be determined made it impossible to correct these values for the PETN present in the detonator.

An undetermined amount of CO₂ was also lost from these traps. We corrected for this by increasing the CO₂ value to give 100% oxygen recovery. This accounts for the 103% carbon recovery shown.

The heat of formation (ΔH_f°) for HNB has not been determined to our knowledge. Using the data from this experiment, we calculated the ΔH_f° to be +15.7 kcal/mol and used this value to calculate the ΔH detonation from the products. This, of course, forces the two ΔH detonation values to agree exactly. The ΔH_f° value we determined agrees well with our estimated value of +18 kcal/mol.

Table 23. Heat and products of detonation of HNB.

Experimental conditions		Detonation
Charge density, g/cm ³		1.918
Percent of TMD		95.9
Charge weight, g		24.9
-ΔH detonation ^a		
Experimental		1653 ± 17
Calculated from products ^b		1653 ± 32
Products, mol/mol HE	N ₂	2.96
	H ₂ O ^c	Not determined
	CO ₂ ^c	5.88
	CO	0.272
	NH ₃ ^c	>0.004
	HCN	0.0077
	NO	0.0068
Material recovery, mol%	C ^c	103
	H ^d	35.3
	N	99.0
	O	100.0

^a 298 K, H₂O(l) (cal/g).

^b This calculation was made using ΔH_f of +15.727 kcal/mol for HNB, calculated from this experiment—thus the exact agreement.

^c Because the stopcocks blew off water traps on warming, the amount of water could not be weighed. An undetermined amount of CO₂ and a very small amount of NH₃ were lost. The CO₂ value was corrected for this loss by increasing it to give 100% oxygen recovery. This resulted in the 103% carbon recovery shown.

^d Hydrogen arises mostly likely from interaction with PETN products. 0.085 g of PETN was used in the detonator.

Hexanitrostilbene (HNS-II)

Rationale. HNS-II was studied under contract to NASA to determine the detonation products produced by a mild detonating fuse containing HNS-II at a density of 1.65 g/cm³. We also studied it at a density of 1.02 g/cm³ because we wished to characterize the material more completely.

Experimental. HNS II (C₁₄H₆N₆O₁₂) was purchased²⁸ and used as received. The material was recrystallized from an organic solvent as

specified by NASA. In the standard detonator described, the 150-mg high-density output pellet was HNS-I rather than PETN. No booster was necessary. The charge at density 1.02 g/cm^3 was pressed in increments directly into the gold cylinder.

Results and Discussion. Results are presented in Table 24; the effect of reducing charge density (i.e., increasing detonation temperature) is clearly evident. There are dramatic increases in CO and H_2 and corresponding decreases in C(s), CO_2 , and H_2O . Material recovery for the low density charge is poorer.

Table 24. Heat and products of detonation of HNS-II at two densities.^a

Experimental conditions		Detonation	Detonation
Charge density, g/cm^3		1.649	1.017
Percent of TMD		94.8	58.4
Charge weight, g		24	15
$-\Delta H$ detonation ^b			
Experimental		1099 $\pm$ 11	878 $\pm$ 9
Calculated from products		968 $\pm$ 120	860 $\pm$ 16
Products, mol/mol HNS-II	N_2	2.76	2.72
	H_2O	1.73	1.29
	CO_2	2.80	1.25
	CO	4.66	8.57
	C(s)	6.38	3.94
	H_2	0.65	1.34
	NH_3	0.21	0.13
	CH_4	0.081	0.16
	HCN	0.084	0.042
	C_2H_6	Not observed	0.013
Material recovery, mol	C	54.6	38.9
	H	96.6	107
	N	97.0	93.4
	O	99.0	103

^a HNS II = $\text{C}_{14}\text{H}_6\text{N}_6\text{O}_{12}$.

^b 298 K, $\text{H}_2\text{O}(\text{l})$ (cal/g).

Hydrazine Nitrate (HN)

Rationale. We studied HN because it is a carbon-free explosive, and we wished to take advantage of this fact in the studies reported in Table 15.

Experimental. The HN ($\text{N}_2\text{H}_4 \cdot \text{HNO}_3$) used in this study was recrystallized from methyl alcohol and dried under vacuum at 40°C . Because products containing carbon were found, the HN was analyzed by GLC and found to contain 3.88 wt% methyl alcohol. We later learned that subjecting molten HN to vacuum reduced the methyl alcohol content to less than 0.01 wt%. The elemental composition was determined by analysis from which we calculated the following empirical formula, adjusting to $\text{N} = 3$: $\text{C}_{0.121}\text{H}_{5.576}\text{N}_{3.000}\text{O}_{3.150}$ (MW = 99.49)

Results and Discussion. Results presented in Table 25 show an unusually large discrepancy between the observed ΔH detonation and that calculated from products. This is surprising because material recoveries of the major elements are reasonably good. The discrepancy remains unexplained. It is noteworthy that water and nitrogen are the only major products.

Hydrazine-Hydrazine Nitrate Explosives

Rationale. These compositions were studied when there was considerable interest in the performance, total energy, and product composition data of this carbon-free system. Reference 3 gives further details.

Experimental. Three liquid systems were studied. RX-23-AA is hydrazine nitrate (HN)/hydrazine (N_2H_4) solution--nominally 79/21 wt%. This system has the maximum energy because only the minimum amount of hydrazine required to dissolve the HN was added. RX-23-AB is $\text{HN}/\text{N}_2\text{H}_4/\text{H}_2\text{O}$ --nominally 70.0/5.9/24.1 wt%. It has the optimum stoichiometric ratio of $\text{HN}/\text{N}_2\text{H}_4$, put into solution with water, and was intended to show the effect of water as a diluent. RX-23-AC is $\text{HN}/\text{N}_2\text{H}_4$ --nominally 30/70 wt%. It has the highest concentration of N_2H_4 that will detonate and was also intended to show the effect of N_2H_4 as a diluent.

Hydrazine nitrate was purified by vacuum sublimation; we have since learned (see Table 25) that this is not the most effective technique.

Table 25. Heat and products of detonation of hydrazine nitrate.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.633
Percent of TMD		98.3
Charge weight, g		23
-ΔH reaction ^b		
Experimental		1247 ± 25
Calculated from products		1459 ± 20
Products, mol/mol HE	N ₂	1.48
	H ₂ O	2.93
	CO ₂	0.0510
	NH ₃	0.0033
	HCN	0.0003
	O ₂	0.0224
	NO	0.0013
	NO ₂	0.0004
Material recovery, mol%	C	49.3
	H	106
	N	98.8
	O	98.1

^a Hydrazine nitrate = C_{0.121}H_{5.567}N_{3.000}O_{3.150} by analysis and adjusted to N = 3.000 (MW = 99.49). Theoretical is H₅N₃O₃. The sample contained 3.88 wt% CH₃OH.

^b 298 K, H₂O(l) (cal/g).

Hydrogen and nitrogen analysis agreed with theory for N₂H₄·HNO₃ within analytical limits. Although the purity of the hydrazine we used was nominally 98%, nuclear magnetic resonance (NMR) analysis indicated that it was 99.3 ± 0.3% pure; water was the principal impurity. Because hydrazine is highly hygroscopic, both water-free mixtures were prepared in a dry box and subsequently handled with minimum exposure to air. The compositions of all mixtures were determined by analysis (Table 26).

PETN boosters were used: 0.5 g for RX-23-AA, 1.0 g for RX-23-AB, and 1.4 g for RX-23-AC. The configuration for liquid explosives described earlier in the experimental section was used. In addition to the usual corrections, results were corrected for the heat of solution of NH₃(g) in H₂O(l) and for the heat of formation of (NH₄)₂CO₃(aq).

Results and Discussion. Results are presented in Table 26. Using water as a diluent in RX-23-AB greatly suppressed ammonia formation; using hydrazine as a diluent in RX-34-AC greatly enhanced ammonia formation. Both of these results were predicted by thermodynamic-hydrodynamic machine calculations. Although material recoveries are not good, we did obtain the principal results sought.

LX-04-1

Rationale. LX-04-1 (HMX/Viton, 85/15 wt%) was studied unconfined in support of the seismic studies program at LLNL.

Table 26. Heats and products of detonation for three hydrazine nitrate/hydrazine explosives.

Experimental conditions	Explosive		
	RX-23-AA, ^a detonation	RX-23-AB, ^b detonation	RX-23-AC, ^c detonation
Charge density, g/cm ³	1.421	1.379	1.153
Charge weight, g	21	20	17
Number of experiments	2	1	3
-ΔH detonation ^d			
Experimental	1340 ± 15	1100 ± 15	980 ± 15
Calculated from products	1405 ± 80	1030 ± 50	1200 ± 200
Products, mol/mol HE			
N ₂	1.64	1.27	1.31
H ₂ O	2.57	3.55	1.31
H ₂	0.12	0.007	0.19
NH ₃	0.49	0.018	2.30
NO	0.0004	0.0003	0.0004
Material recovery, mol%			
H	111	108	101
N	98.4	102	93.5
O	102	98	113

^a Hydrazine nitrate/hydrazine (78.42/21.58 wt% by analysis);
H_{6.22}N_{3.84}O_{2.50} (MW = 100).

^b Hydrazine nitrate/hydrazine/water (69.02/5.08/25.90 wt% by analysis);
H_{6.62}N_{2.51}O_{3.63} (MW = 100).

^c Hydrazine nitrate/hydrazine (32.45/67.55 wt% by analysis);
H_{9.89}N_{5.22}O_{1.06} (MW = 100).

^d 298 K, H₂O(l) (cal/g).

Experimental. The LX-04-1 used was production grade. The charge was spherical and unconfined to duplicate the conditions used in seismic studies. Unconfined charges do not yield heats and products of detonation, as described earlier.

Results and Discussion. Results are presented in Table 27. The charge size of 5.6 g was considerably less than usual. It is noteworthy that HF was the only product detected that contained fluorine, which confirms other work presented in this report. The very poor fluorine recovery resulted from the fact that the experiment was conducted in the stainless steel bomb rather than the Monel bomb. The very good agreement between the experimental ΔH and that calculated from the products was fortuitous.

Table 27. Heat and products of reaction of unconfined LX-04-1.^a

Experimental conditions		Reaction
Charge configuration		Unconfined sphere
Charge density, g/cm ³		1.86
Charge diameter, mm		19.1
Charge weight, g		5.6
- ΔH reaction ^b		
Experimental		1119 $\pm$ 11
Calculated from products		1119 $\pm$ 16
Products, mol/mol LX-04-1	N ₂	1.14
	H ₂ O	0.59
	CO ₂	0.26
	CO	1.31
	H ₂	0.61
	NH ₃	0.0024
	HF	0.52 ^c
Material recovery, mol%	C	101
	H	96.5
	N	99.5
	O	105
	F	14

^a LX-04-1 (HMX/Viton-A, 85/15 wt%); C_{1.55}H_{2.58}N_{2.30}O_{2.30}F_{0.52} (MW = 100).

^b 298 K, H₂O(l) (cal/g).

^c Determined from the total fluorine in LX-04-1. No other products containing fluorine were detected.

LX-11-0

Rationale. LX-11-0 (HMX/Viton, nominally 80/20 wt%) was studied as part of a continuing program to evaluate the suitability and applicability of thermodynamic-hydrodynamic codes that predict detonation parameters. Calculations indicated that with a 20% Viton loading, CF_4 would be present in the products below the freeze-out temperature. Reference 3 gives further details.

Experimental. LX-11-0 (80.1/19.9 wt% by analysis), $\text{C}_{1.61}\text{H}_{2.54}\text{N}_{2.16}\text{O}_{2.16}\text{F}_{0.69}$ (MW = 100), was studied using a Monel bomb and the special HF traps. Because a significant amount of water was expected (which would retain all the HF in the traps), potassium fluoride was not needed in the traps. PETN boosters (0.3 g) were needed in addition to the standard detonator. Results were corrected for the reaction of HF with Monel 400 and for the heat of formation of $\text{NH}_4\text{F}(\text{aq})$ and $\text{HF}(\text{g})$.

Results and Discussion. Results are presented in Table 28. As predicted, a very small amount of CF_4 was observed in the products. Once again, the high-temperature, low-pressure equilibration of products from unconfined charges shows up as a reduction in ΔH reaction, reduced amounts of H_2O , $\text{C}(\text{s})$, and CO_2 , and increased amounts of CO and H_2 . We note that CF_4 was not detected in the unconfined experiment as expected because of lower-pressure equilibration conditions. Material recoveries are generally good except for that of fluorine, which, in the form of HF, is assumed to react with Monel metal. The products in Table 28 are corrected for this reaction, as indicated above.

Nitromethane (NM)

Rationale. NM was studied as one of a carefully selected series of explosives of differing elemental composition, density, and physical state for which performance and product composition data were desired. It was also used to optimize the experimental configuration that would yield ΔH detonation and products most representative of CJ isentropic expansion. Part of this work has been reported elsewhere.²

Table 28. Heat and products of detonation of LX-11-0.^a

Experimental conditions		Confined, detonation	Unconfined, reaction
Charge density, g/cm ³		1.89	1.88
Percent of TMD		99.5	99.5
Charge diameter, mm		12.7	25.4
Charge weight, g		25	25
Number of experiments		1	2
-ΔH reaction ^b			
Experimental		1124 ± 40	870 ± 40
Calculated from products		1262 ± 100	987 ± 80
Products, mol/mol LX-11-0	N ₂	0.98	1.07
	H ₂ O	0.70	0.40
	CO ₂	0.59	0.22
	CO	0.34	1.38
	C(s)	0.67	Not detected
	H ₂	0.038	0.53
	NH ₃	0.093	0.0003
	CH ₄	0.009	Not detected
	HCN	0.003	0.0002
	HF(g) ^c	0.65	0.69
	CF ₄	0.010	Not detected
	C ₂ H ₆	0.001	Not detected
Material recovery, mol%	C	58.9	99.1
	H	92.5	101
	N	95.2	98.4
	O	102	102
	F ^d	94.1	83.1

^a HMX/Viton (80.1/19.9 wt%), by analysis: C_{1.61}H_{2.54}N_{2.16}O_{2.16}F_{0.69}, (MW = 100).

^b 298 K, H₂O(l), HF(g) (cal/g).

^c From the total fluorine contained in LX-11-0 less that found as CF₄.

^d Fluorine recovered as products plus detectable metal fluoride.

Experimental. Commercial grade NM (CH₃NO₂) was used. GLC showed a purity of 96.7 wt%; impurities were nitroethane (0.94%), 1-nitropropane (0.03%), 2-nitropropane (2.5%), and water (0.1%). The empirical formula on which results are based, C_{1.000}H_{2.959}N_{0.959}O_{1.918} (MW = 59.11), was calculated from this analysis.

The configuration described earlier for liquid explosives was used. We deaerated NM by freezing it in a sealed container with liquid nitrogen,

evacuating the container, resealing the container, and melting the NM; this procedure was repeated several times. Deaeration prevents formation of an undesirable air bubble (which acts as an attenuator) between the booster and liquid main charge when the bomb is evacuated. PETN boosters (0.75 g) were needed for initiation.

Nitromethane (and TNT, Table 44) were used in studies to optimize the experimental configuration. Each explosive was used separately as described in the experimental section of this report.

Results and Discussion. Results are presented in Table 29. The experiment with end confinement shows increases in the heat of detonation and in the species representative of a lower-temperature isentrope--C(s), H₂O, and CO₂--and corresponding decreases in the species representative of a higher temperature isentrope--CO and H₂--when the two isentropes are compared at the same volume.

Nitromethane/Nitropropane/Ethylenediamine

Rationale. Nitromethane/2-nitropropane/ethylenediamine (NM/NP/ED) was studied at a 1:1 mol ratio of NM:NP, which is balanced to H₂O and C(s). This is the water counterpart of 1,2-bis-(difluoroamino) propane (Table 10) that is balanced to HF and C(s). Comparison of performance and product composition data provides information on the relative merits of H₂O vs HF as principal products.

Experimental. The mixture was NM/NP/ED (38.63/56.37/5.00 wt%); the empirical formula is C_{2.70}H_{6.99}N_{1.43}O_{2.53} (MW = 100). Commercial quality materials were used: NM purity was as described above, NP was 97% minimum (by GLC according to the manufacturer's label), and ED was 99+% pure (according to the manufacturers label).

The configuration described in the experimental section for liquid explosives was used. A PETN booster (0.5 g) was needed.

Results and Discussion. Results are presented in Table 30. Although nearly balanced to H₂O and C(s), large amounts of other lower-energy products containing hydrogen and oxygen were produced, which complicated comparing the effects of H₂O generated in this experiment with those of the HF produced by

Table 29. Heat and products of detonation of nitromethane.^a

Experimental conditions	Cylinder confinement	
	Ends closed, detonation	Ends open, detonation
Charge density, g/cm ³	1.13	1.13
Charge weight, g	15	18
Number of experiments	1	2
-ΔH reaction ^b		
Experimental	1227 ± 12	1181 ± 12
Calculated from products	1254 ± 13	1231 ± 40
Products, mol/mol NM		
N ₂	0.39	0.41
H ₂ O	0.88	0.86
CO ₂	0.26	0.24
CO	0.55	0.64
C(s)	0.095	0.045
H ₂	0.29	0.31
NH ₃	0.12	0.08
CH ₄	0.083	0.068
HCN	0.0081	0.0048
C ₂ H ₆	0.001	0.001
C ₂ H ₄	Not detected	0.0022
C ₂ H ₂	0.001	Not detected
Material recovery, mol%		
C	91.5	95.2
H	103	103
N	96.2	94.2
O	103	103

^a NM = C_{1.000}H_{2.959}N_{0.959}O_{1.918} by analysis and adjusted to C = 1 (MW = 59.11).

^b 298 K, H₂O(l) (cal/g).

detonation of 1,2-bis(difluoroamino) propane (Table 10). We obtained a better comparison when cylinder test data was included. Material balances for hydrogen and nitrogen were low, as is usual for explosives that produce solid carbon.

Octol

Rationale. Octol was studied as part of an LLNL project to investigate the interaction between mixtures of ideal explosives.

Table 30. Heat and products of detonation of NM/NP/ED.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.003
Charge weight, g		14.9
-ΔH reaction ^b		
Experimental		1060 ± 11
Calculated from products		990 ± 60
Products, mol/mol HE	N ₂	0.312
	H ₂ O	1.36
	CO ₂	0.327
	CO	0.427
	C(s)	1.57
	H ₂	0.350
	NH ₃	0.516
	CH ₄	0.316
	HCN	0.046
	NO	0.040
	NO ₂	0.040
	C ₂ H ₆	0.0049
	C ₂ H ₄	0.0016
	C ₂ H ₂	0.0005
Material recovery, mol%	C	41.9
	H	90.5
	N	88.9
	O	103

^a NM/NP/ED (38.63/56.37/5.00 wt%) C_{2.70}H_{6.99}N_{1.43}O_{2.53} (MW = 100).

^b 298 K, H₂O(l) (cal/g).

Experimental. Octol is HMX/TNT (73.58/26.42 wt% by analysis) from which we calculated an empirical formula of C_{1.808}H_{2.569}N_{2.336}O_{2.685} (MW = 100). We used military grade octol that had been jar milled to produce particles less than 1 mm in diameter.

Results and Discussion. Results are presented in Table 31. The heat of detonation calculated from the products agreed very well with the observed value. The hydrogen and nitrogen material recoveries were very good for an explosive that produces solid carbon. As expected, the heat of detonation and products of detonation of octol were between the values for TNT and HMX when compared on an equal weight basis.

Pentaerythritol Tetranitrate (PETN)

Rationale. PETN was the first explosive to be studied in the 25-g calorimeter described here. It was studied from 1962 to 1965. It was chosen because it is contained in our standard detonator, and a reliable heat-of-detonation value and a knowledge of product composition were essential. Reference 1 gives further details.

Experimental. PETN ($C_5H_8N_4O_{12}$) was studied in a variety of configurations. Two types of PETN were studied: detonator grade (war reserve²⁹) and a special high-purity grade³⁰ meeting Military Specification MIL-P-387A. The purities of these explosives were checked by mp and TLC measurements. Detonator-grade

Table 31. Heat and products of detonation of octol.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.81
Percent of TMD		99.0
Charge weight, g		26.2
-ΔH detonation ^b		
Experimental		1361 ± 14
Calculated from products		1387 ± 18
Products, mol/mol octol	N ₂	1.08
	H ₂ O	0.852
	CO ₂	0.643
	CO	0.522
	C(s)	0.617
	H ₂	0.146
	NH ₃	0.135
	CH ₄	0.025
	HCN	0.014
	C ₂ H ₆	0.004
Material recovery, mol%	C	66.1
	H	98.1
	N	98.5
	O	99.1

^a Octol is HMX/TNT (73.58/26.42 wt% by analysis). The empirical formula is $C_{1.808}H_{2.569}N_{2.336}O_{2.685}$ (MW = 100).

^b 298 K, H₂O(l) (cal/g).

PETN (mp 140.6-141.6°C) contained about 1% impurities, which analysis showed to be pentaerythritol trinitrate (Petrin), dipentaerythritol hexanitrate, trientaerythritol octanitrate, and trace amounts of an unidentified material. High-purity PETN (mp 141.6-142.2°C) contained less than 1% impurities, which were Petrin and trace amounts of an unidentified material.

In an attempt to learn more about product freeze-out, PETN was also fired in an oxygen atmosphere balanced to H_2O and CO_2 . It was also fired in various metal confinement cylinders to determine the effect of the metal and to determine if the PETN products would oxidize the metal.

Results and Discussion. Corrected results of the basic PETN study are presented in Table 32; eleven other experiments were conducted in addition to those shown. In these shots, the density as well as the confinement of the charges were varied. The products from the lightly confined charges were reshocked above the freeze-out temperature; hence, the products reequilibrated, and any observable effects caused by variations in density or light confinement were eliminated. These results are not reported.

When material balances were calculated, a loss of oxygen was found for all experiments. This loss ranged from a minimum of 0.3 to 0.5 mol% for heavily confined charges and 1% for unconfined charges to a maximum of 11 mol% for lightly confined (0.013-cm-thick gold) charges. We attribute the oxygen loss to reactions between detonation products and stainless steel. The results for unconfined charges shown in Table 32 were corrected for these reactions by plotting products or ΔH against oxygen loss for unconfined or lightly confined tests and extrapolating to zero oxygen loss. Corrections amounted to 2 cal/g for ΔH and averaged 0.05 mol of product per mol PETN. The heavily confined results shown in Table 32 are not corrected for metal reactions because the oxygen-loss corrections would be insignificant.

The differences in heat and products between heavily confined and unconfined charges, between charges at different densities, and between the different types of PETN are small and essentially within experimental error. The exception is CO for which the analytical method is least accurate. It is noteworthy that small amounts of NH_3 and CH_4 were found in the detonation products of heavily confined charges but not in the unconfined charges. As expected, no solid carbon was observed. PETN is slightly under-balanced to H_2O and CO_2 . For a CO_2 -balanced explosive, we expect that the heat and products of detonation will not change as confinement or density change.

From the data in Table 32, the average ΔH detonation of PETN is 1490 ± 5 cal/g, and a representative product distribution is given in column 1 of Table 32.

Another study of high-purity PETN was conducted using the standard 12.7-cm-diam heavily confined configuration in which the confining cylinder was made of copper, nickel, or lead. We sought to find an acceptable replacement for gold to contain larger charges fired in a 1.2-m-diam detonation sphere at Site 300; these experiments were designed to determine product composition only.

Table 33 compares the products obtained using confinement cylinders made from the different metals. None of the metals significantly changed the ΔH detonation although slight shifts in the product distributions appeared that

Table 33. Effects of using various metals for confinement on the heat and products of detonation of PETN.^a

Experimental conditions	Metal confinement			
	Gold, detonation	Copper, detonation	Nickel, detonation	Lead, detonation
Number of experiments	3	1	1	1
- ΔH detonation ^b				
Experimental	1490 $\pm$ 5	1485	1476	1493
Calculated from products	1501 $\pm$ 11	1536 $\pm$ 15	1532 $\pm$ 15	1498 $\pm$ 1
Products, mol/mol PETN				
N ₂	2.00 $\pm$ 0.02	1.92	1.94	1.97
H ₂ O	3.50 $\pm$ 0.05	3.64	3.65	3.39
CO ₂	3.39 $\pm$ 0.04	3.41	3.41	3.46
CO	1.69 $\pm$ 0.03	1.67	1.63	1.69
H ₂	0.45 $\pm$ 0.01	0.33	0.33	0.35
NH ₃	0.038 $\pm$ 0.006	0.065	0.047	0.071
CH ₄	0.003 $\pm$ 0.001	0.002	0.004	0.004
Material recovery, mol%				
C	101.5 $\pm$ 0.5	102	101	98.0 ^c
H	100 $\pm$ 1	102	101	91.7
N	101 $\pm$ 1	97.6	98.5	95.5
O	100 $\pm$ 1	101	101	95.1

^a Charge density = 1.69 to 1.72 g/cm³; charge weight = 25 g.

^b 298 K, H₂O(l) (cal/g).

^c Low material balances resulted from incomplete removal of products, which was caused by lead partial blocking the gas-removal port.

were beyond experimental error. Although the product values with lead confinement are closest to those with gold confinement, the material recovery was incomplete because the valve in the calorimeter lid (B, Fig. 2) was blocked by a thick layer of lead that coated the entire inside surface of the calorimeter bomb; this lead coating was removed from the bomb only by heating the bomb to melt the lead.

On the basis of these results, we chose copper as the confining metal for charges fired in the large detonation sphere. We found that copper fragments are slightly discolored after an experiment, indicating some oxidation, but this does not affect the material recovery.

A third study was made with high-purity PETN. Machine calculations indicate that the freeze-out temperature range of 1500-1800 K occurs at 1-2 relative volumes. As a result of such small expansion, the products from a heavily confined shot should still be contained within the gold cylinder and should not equilibrate with a potentially reactive oxygen atmosphere in the bomb. PETN (and TNT, Table 44) were fired in oxygen atmospheres. They represent the extremes in terms of the amount of solid carbon present in the products.

The PETN results (Table 34) show essentially complete reaction, which gives an energy value close to the heat of combustion for PETN (1957 cal/g). We postulate that if only a very small amount of products escaping from the cylinder is hot enough to react with oxygen, this reaction will increase the overall temperature to a point that complete interaction between products and oxygen occurs. The work with TNT (Table 44) provides more data on this subject.

RX-04-DS

Rationale. RX-04-DS (HMX/Al/Viton) was one of a series of aluminized explosives for which performance measurements were made in an overall study of composite explosives. Thermodynamic-hydrodynamic calculations indicated that for HMX-aluminum compositions containing about 10% Viton as a binder, maximum performance would be realized with 7-12 vol% aluminum. RX-04-DS contains 7.1 vol% aluminum (particle size of 5 μ m). Both the total energy released and the disposition of aluminum and fluorine in the detonation products were of interest.

Table 34. Results of detonating heavily confined PETN^a charges in various atmospheres.

Experimental conditions		Atmosphere	
		Vacuum, detonation	Oxygen, detonation
Charge density, g/cm ³		1.73-1.74	1.70
Balance level attempted		-	CO ₂ + H ₂ O
Pressure, atm (absolute)		0	0.38
Number of experiments		3	1
-ΔH detonation ^b			
Experimental		1490 ± 5	1916 ± 5
Calculated from products		1513 ± 20	1908 ± 10
Products, mol/mol TNT	N ₂	2.00	2.00
	H ₂ O	3.50	4.01
	CO ₂	3.39	4.83
	CO	1.69	0.15
	H ₂	0.45	0.035
	NH ₃	0.038	0.007
	CH ₄	0.003	Not detected
Material recovery, mol%	C	101.5	99.6
	H	100.1	101.3
	N	100.8	100.3
	O	99.7	98.5

^a Charge weight = 22.5 to 25 g.

^b 298 K, H₂O(l) (cal/g).

Experimental. RX-04-DS (HMX/Al/Viton, 81.0/9.9/9.1 wt% by analysis) with the empirical formula C_{1.34}H_{2.36}N_{2.19}O_{2.19}F_{0.316}Al_{0.367} (MW = 100) was studied using the Monel bomb. Determination of all products shown in Table 35 was a difficult process. Aluminum found in solution in the bomb wash was assumed to be AlF₃. One means of determining Al₂O₃ was to subtract the AlF₃ from the total aluminum in the system. A second means was to assume that oxygen not accounted for in the material recovery had combined with aluminum to form Al₂O₃. The two methods agreed well, and we used the average value. Ammonia found in the bomb was assumed to be present as NH₄F. The fluoride ion in the bomb wash in excess of that attributable to

NH_4F should be from AlF_3 , and this amount was in reasonable agreement with the amount of aluminum found in the wash solution. Note that only about 12% of fluorine was recovered, of which 99% came from the bomb washings and only 1% came from the water traps (where it should appear if present in the form of HF). We concluded that most of the HF reacted with the Monel metal in the bomb. NiF_2 and CuF are slightly soluble in water, and these metal fluorides should therefore contribute very little to the fluorine in solution; we found only traces of Ni and Cu in solution.

Results and Discussion. The results presented in Table 35 are corrected for the reactions of HF with Monel metal and for the formation of NH_4F . Most of the fluorine appears as HF and most of the aluminum as Al_2O_3 .

RX-08-EP

Rationale. RX-08-EP (HMX/FEFO/SiO_2) is a paste explosive developed for a nuclear weapon application. The heat and products of detonation were determined as part of the characterization of the explosive. We had not previously studied a paste explosive having a practical application.

Experimental. RX-08-EP (73.3/25.2/1.5 wt%, respectively, of the components listed above) was formulated at LLNL and loaded into the gold cylinder under vacuum using a deaerator loader. Cab-O-Sil (SiO_2) was present to stabilize the paste. We used the standard charge configuration for solids described in the experimental section. The empirical formula based on the analyzed composition given above is $\text{C}_{1.384}\text{H}_{2.452}\text{H}_{2.295}\text{O}_{2.767}\text{F}_{0.157}(\text{SiO}_2)_{0.0253}$; SiO_2 is represented in this way because it does not take part in the detonation reaction. The Monel bomb and HF- H_2O traps were used.

Results and Discussion. The results are presented in Table 36. As expected, HF was clearly established as the only product containing fluorine. The heat and products of detonation were corrected for the reaction of HF with NH_3 to form NH_4Cl and with Monel to form NiF_2 . As expected, nitrogen recovery was low, but hydrogen recovery was surprisingly high. HF could not be recovered quantitatively, so its value was set equal to the amount of fluorine present in the explosive. The agreement between the corrected observed heat

Table 35. Heat and products of detonation of RX-04-DS.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.933
Percent of TMD		99.2
Charge weight, g		25
Number of experiments		2
-ΔH detonation ^b		
Experimental		1600 ± 25
Calculated from products		1545 ± 30
Products, mol/mol HE	N ₂	1.02
	H ₂ O	0.52
	CO ₂	0.24
	CO	0.75
	C(s)	0.31
	H ₂	0.18
	NH ₃	0.081
	CH ₄	0.038
	HCN	0.008
	HF ^c	0.30
	Al ₂ O ₃	0.17
	AlF ₃ ^d	0.0045
Material recovery, mol%	C	77
	H	82
	N	98
	O ^e	80
	F	12
	Al ^e	1

^a RX-04-DS = C_{1.34}H_{2.36}N_{2.19}O_{2.19}F_{0.316}Al_{0.367} (MW = 100).

^b 298 K, H₂O(l) (cal/g).

^c From total fluorine less AlF₃ found.

^d From aluminum found in solution in bomb wash.

^e Does not include contribution from Al₂O₃.

of detonation and that calculated from the corrected products is reasonably good considering the difficulties encountered during some analyses.

RX-22-AG

Rationale. RX-22-AG (HMX/LiClO₄, 81.7/18.3 wt%) was one of the most energetic and novel in a series of composite explosives we studied. Total energy and the disposition of lithium and chlorine in the products were of principal interest.

Table 36. The heat and products of detonation of RX-08-EP.^a

Experimental conditions		Detonation
Charge density, g/cm ³		2.19
Percent of TMD		~100
Charge weight, g		27
-ΔH detonation ^b		
Experimental		1357 ± 14
Calculated from products		1404 ± 35
Products, mol/mol HE	N ₂	1.009
	H ₂ O	0.946
	CO ₂	0.684
	CO	0.402
	C(s)	0.285
	H ₂	0.087
	NH ₃	0.140
	CH ₄	0.009
	HCN	0.003
	HF ^c	0.157
	C ₃ H ₈	0.0001
Material recovery, mol%	C	79.4
	H	110
	N	94.2
	O	98.2
	F ^c	100

^a RX-08-EP is HMX/FEFO/SiO₂ (73.30/25.19/1.51 wt% by analysis). The empirical formula is C_{1.384}H_{2.452}N_{2.295}O_{2.767}F_{0.157}(SiO₂)_{0.0253} (MW = 100).

^b 298 K, H₂O(l) (cal/g). Corrected for reaction of HF with NH₃ to form NH₄F and with Monel to form NiF₂.

^c The product HF could not be recovered quantitatively. HF was set equal to the amount of fluorine that was present in the explosive.

Experimental. The intent was to formulate HMX/LiClO₄ (74/26 wt%) that is CO₂ balanced. Analysis of the mixture gave the composition shown above; the empirical formula is C_{1.10}H_{2.21}N_{2.21}O_{2.90}Cl_{0.17}Li_{0.17} (MW = 100). Because LiClO₄ is highly hygroscopic, the charge was prepared by mixing and pressing in a dry box. The particle size of the LiClO₄ was about 1 μm. The amount of LiCl in the products was determined by wet analyses of the bomb wash for lithium and chloride ions and taking the mean of the two values; these values differed by only 0.05%.

Results and Discussion. Results are presented in Table 37. Our observations lead us to conclude that LiCl is the only product containing lithium and chlorine.

RX-25-BF

Rationale. RX-25-BF ($\text{ZrH}_2/\text{NH}_4\text{ClO}_4/\text{HMX}/\text{estane}$) was developed as a shaped-charge explosive under a non-nuclear ordnance project, and we studied it to improve our understanding of the interaction of fuel and oxidizer in composite explosives. The unusual fuel, ZrH_2 , was of particular interest.

Table 37. Heat and products of detonation of RX-22-AG.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.91
Percent of TMD		96.5
Charge weight, g		24.4
-ΔH detonation ^b		
Experimental		1635 ± 16
Calculated from products		1558 ± 60
Products, mol/mol HE	N ₂	1.05
	H ₂ O	0.97
	CO ₂	0.85
	CO	0.19
	C(s)	0.057
	H ₂	0.04
	NH ₃	0.032
	CH ₄	0.002
	LiCl	0.17
	O ₂	0.002
Material recovery, mol%	C	94.9
	H	96.8
	N	97.1
	O	99.5
	Li	96.3
	Cl	96.8

^a RX-22-AG (HMX/LiClO₄, 81.7/18.3 wt%), C_{1.10}H_{2.21}N_{2.21}O_{2.90} Cl_{0.17}Li₀. (MW = 100).

^b 298 K, H₂O(l) (cal/g).

Experimental. RX-25-BF (22.1/36.9/37.0/4.0 wt%, respectively, of the components listed above) was formulated at LLNL. The ZrH_2/AP ratio was stoichiometric to ZrO_2 , HCl , and H_2O before adding the HMX and estane. The empirical formula based on the analyzed composition given above is $\text{C}_{0.709}\text{H}_{3.015}\text{N}_{1.321}\text{O}_{2.327}\text{Zr}_{0.237}\text{Cl}_{0.314}$ (MW = 100).

Results and Discussion. Results are presented in Table 38. HCl and ZrO_2 were clearly established as the only products containing chlorine and zirconium, respectively. The heat and products of detonation were corrected for the reaction of HCl with NH_3 to form NH_4Cl and with stainless steel to form FeCl_2 . Hydrogen recovery was low, but the nitrogen recovery was unusually good for an explosive that produces solid carbon. HCl and ZrO_2 could not be recovered quantitatively. Their values were set equal to the amounts of chlorine and zirconium, respectively, that were present in the explosive. The agreement between the corrected observed heat of detonation and that calculated from the corrected products was not as good as for most other explosives. The problem is related to the large number of detonation products, some of which are determined only with difficulty.

RX-36 Explosives

Rationale. RX-36 explosives were a series of mixtures of HMX/BTF/TATB studied to determine the effects of detonation temperature on the working fluid. The matrix involved seven mixtures in which the mol ratios of the components were varied to hold either the temperature constant and vary the gas volume (working fluid) or hold the gas volume constant and vary the temperature.

Experimental. RX-36-AA is HMX/BTF/TATB (1:1:1 mol ratio, 34.56/32.21/33.23 wt% by analysis) and has an empirical formula of $\text{C}_{2.006}\text{H}_{1.682}\text{N}_{2.473}\text{O}_{2.473}$ (MW = 100). RX-36-AF is HMX/TATB (1:1 mol ratio, 53.51/46.49 wt% by analysis) and has an empirical formula of $\text{C}_{1.804}\text{H}_{2.527}\text{N}_{2.527}\text{O}_{2.527}$ (MW = 100). The HMX was class B, the TATB was material designated as superfine, and the BTF was commercially produced¹⁷ and purified at LLNL.

Results and Discussion. Results are presented in Table 39. The heats of detonation calculated from the products did not agree well with the observed

Table 38. The heat and products of detonation of RX-25-BF.^a

Experimental conditions		Detonation
Charge density, g/cm ³		2.15
Percent of TMD		98.3
Charge weight, ^b g		24.2
-ΔH detonation ^c		
Experimental		1247 ± 25
Calculated from products		1369 ± 100
Products, mol/mol HE		
	N ₂	0.640
	H ₂ O	0.902
	CO ₂	0.331
	CO	0.316
	C(s)	0.0467
	H ₂	0.222
	NH ₃	0.0433
	CH ₄	0.0067
	HCN	0.0066
	HCl	0.313
	NO	0.00025
	C ₃ H ₈	0.00055
	C ₃ H ₆	0.00025
	ZrO ₂	0.237
Material recovery, mol%		
	C	93.5
	H	90.5
	N	101
	O	101
	Zr ^d	100
	Cl ^d	100

^a RX-25-BF is ZrH₂/NH₄ClO₄/HMX/Estane (22.1/36.9/37.0/4.0 wt% by analysis. The empirical formula is C_{0.709}H_{3.015}N_{1.321}O_{2.327}Zr_{0.237}Cl_{0.314} (MW = 100).

^b Charge length is 89 mm instead of the usual 114 mm.

^c 298 K, H₂O(l) (cal/g). Corrected for reaction of HCl with NH₃ to form NH₄Cl and with stainless steel to form FeCl₂.

^d The products HCl and ZrO₂ could not be recovered quantitatively. They were set equal to the amount of chlorine and zirconium that was present in explosive.

value. Material recoveries were generally poor. Because we studied only t of the seven explosives in the matrix, we could not draw any conclusions concerning the effects of temperature and gas volume.

Table 39. Heat and products of detonation of RX-36 explosives.

Experimental conditions	Explosive	
	AA, ^a detonation	AF, ^b detonation
Mol ratio (HMX/TATB/BTF)	1/1/1	1/1/0
Charge density, g/cm ³	1.813	1.812
Percent of TMD	94.8	94.5
Charge weight, g	26.3	26.2
-ΔH detonation ^c		
Experimental	1291 ± 13	1267 ± 13
Calculated from products	1169 ± 110	1015 ± 240
Products, mol/mol NM		
N ₂	1.034	1.096
H ₂ O	0.573	0.883
CO ₂	0.588	0.645
CO	0.554	0.323
C(s)	0.835	0.678
H ₂	0.094	0.0919
NH ₃	0.093	0.147
CH ₄	0.013	0.0191
HCN	0.017	0.0143
CH ₂ O	0	0.0002
Material recovery, mol%		
C	58.6	59.7
H	100	93.8
N	88.1	92.6
O	93.1	96.8

^a RX-36-AA is HMX/TATB/BTF (34.56/32.21/33.23 wt% by analysis). The empirical formula is C_{2.006}H_{1.682}N_{2.473}O_{2.473} (MW = 100).

^b RX-36-AF is HMX/TATB/BTF (53.51/46.49 wt% by analysis). The empirical formula is C_{1.804}H_{2.527}N_{2.527}O_{2.527} (MW = 100).

^c 298 K, H₂O(l) (cal/g).

Tetranitromethane/Aluminum (TNM/Al)

Rationale. TNM/Al was studied as part of a study of the fluorine oxidizer program funded by the Office of Naval Research in which we compared the effects of the detonation products Al₂O₃ vs AlF₃ on explosive performance.

Experimental. The composition of the TNM/Al mixture that is balanced to Al₂O₃ and CO₂ is 64.50/35.50 wt%. However, after the shot was fired,

analysis of the starting aluminum (Alcoa 1660 flake; particle size 3-65 μm) showed it was 86.5% active aluminum. The composition was recalculated at 67.7/32.3 wt%, which meant it had been over-balanced in oxygen to Al_2O_3 and CO_2 . The empirical formula was $\text{C}_{0.345}\text{N}_{1.38}\text{O}_{2.77}\text{Al}_{1.20}$ (MW = 100).

The TNM used was commercial quality.²⁷ The configuration for liquid explosives previously described was used. A 0.5-g PETN booster was needed to initiate the main charge.

Results and Discussion. Results are given in Table 40. This explosive gave the highest ΔH detonation we have ever observed. The presence of hydrogen-containing species in the products indicates that there were impurities in one or both of the reactants. The combination of high hydrogen

Table 40. Heat and products of detonation of TNM/Al.^a

Experimental conditions		Detonation
Charge density, g/cm^3		1.828
Percent of TMD		95.5
Charge weight, g		26
$-\Delta H$ detonation ^b		
Experimental		2773 ± 28
Calculated from products		2641 ± 46
Products, mol/mol HE	N_2	0.63
	H_2O	0.089
	CO_2	0.27
	CO	0.12
	H_2	0.015
	NH_3	0.0007
	HCN	0.0003
	Al_2O_3^c	0.60
	NO	0.0001
	NO_2	0.0001
Material recovery, mol%	C	112
	H	393
	N	90.9
	O	92.5
	Al	0

^a TNM/Al (67.7/32.3 wt% by analysis). $\text{C}_{0.345}\text{N}_{1.38}\text{O}_{2.77}\text{Al}_{1.20}$ (MW = 100).

^b 298 K, $\text{H}_2\text{O}(\text{l})$ (cal/g).

^c Determined from aluminum in mixture.

and low oxygen recoveries ruled out the possibility that a significant amount of water of hydration was associated with the Al_2O_3 that coated the aluminum surface.

Analysis of the solid residue in the bomb showed only 0.2% active aluminum; we thus concluded that all of the aluminum reacted.

Tetranitromethane/Carbon (TNM/C)

Rationale. TNM/C was studied under funding by the Office of Naval Research in an effort to better understand the interaction of fuel and oxidizer in composite explosives. Because the oxidizer was a liquid, this composition was considered to have the most intimate mixing.

Experimental. TNM/C (84.5/15.5 wt%) is a stoichiometric ratio to produce CO_2 and N_2 . Cab-O-Sil (SiO_2), 1.5 wt%, was added to make a stable gel, but it does not react chemically. The empirical formula is $\text{C}_{1.711}\text{N}_{1.710}\text{O}_{3.469}$ (MW = 100). We purchased both the TNM²⁷ and the carbon.³¹ According to the manufacturer's specifications, the carbon was graphite, -325 mesh, and 99.99+% pure.

The configuration described earlier for liquid explosives was used. A 0.5-g PETN booster was required.

Results and Discussion. Results are presented in Table 41. The data clearly indicate that essentially all the carbon reacted to produce CO_2 . For a CO_2 -balanced explosive, the material recovery and the agreement between the heat of detonation calculated from products and the observed value were both significantly poorer than expected.

Triaminotrinitrobenzene (TATB)

Rationale. Because of the current interest in insensitive, thermally stable high explosives, much effort has been expended in obtaining performance data on TATB. The heat and products of detonation were of interest as part of this performance data.

Experimental. The TATB used was manufactured by Cordova³² and had a total chlorine content of 0.72 wt%. Assuming that the chlorine found was NH_4Cl

Table 41. Heat and products of detonation of TNM/C.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.67
Percent of TMD		96.3
Charge weight, g		24
-ΔH detonation ^b		
Experimental		1602 ± 16
Calculated from products		1528 ± 60
Products, mol/mol HE	N ₂	0.797
	CO ₂	1.568
	CO	0.00994
	HGN ^c	0.00058
	NO	0.0216
Material recovery, mol%	C	93.4
	H	95.4
	O	91.2

^a Composition by formulation. The empirical formula is C_{1.711}N_{1.710}O_{3.4} (MW = 100).

^b 298 K (cal/g).

^c Hydrogen came from PETN.

and adjusting C = 6, the empirical formula is C_{6.000}H_{6.203}N_{6.050}O_{6.000}Cl₀. (MW = 260.84). It was normal production-grade material. In addition to standard detonator, a 0.75-g PETN booster was used.

Results and Discussion. Results appear in Table 42. As expected for such low-oxygen-balanced explosive, a very large amount of solid carbon was produced. The very low amount of CO might be surprising unless one considers the very low calculated detonation temperature of about 2200 K. Material recovery was poor (particularly for hydrogen and nitrogen), which has been observed many times before with explosives that produce large amounts of carbon (see Table 14, bitetrazole). We considered these results rather and hope to repeat this experiment to obtain better data.

2,4,6-Trinitrotoluene (TNT)

Rationale. TNT was studied as the lowest oxygen-balanced explosive in carefully selected series of explosives of differing oxygen balance and

elemental composition. The heats and products of detonation of low-oxygen-balanced explosives are sensitive to variations in confinement. TNT was therefore used in some studies in which the amount and material of confinement was varied. This work is reported in part elsewhere.²

Experimental. The TNT used was Military Specification, Grade III. We used LLL Sample A-202 for the work listed in columns 1, 4, and 5 of Table 43 and in Tables 44 and 45, which was done in 1966-7. We used LLL Sample A-530, a more recent lot, for the work in the remainder of the columns in Table 43. Analysis of Sample A-202 by TLC showed less than 2% impurities, which were identified as 2,4,5-trinitrotoluene, 2,4-dinitrotoluene, and trinitrobenzoic

Table 42. Heat and products of detonation of TATB.^a

Experimental conditions		Detonation
Charge density, g/cm ³		1.87
Percent of TMD		96.5
Charge weight, g		24
-ΔH detonation ^b		
Experimental		1018 ± 10
Calculated from products		1022 ± 18
Products, mol/mol TATB		
	N ₂	2.34
	H ₂ O	2.08
	CO ₂	1.95
	CO	0.40
	C(s)	3.61
	H ₂	0.086
	NH ₃	0.11
	CH ₄	0.026
	HCN	0.014
	HCl ^c	0.050
Material recovery, mol%		
	C	41.5
	H	78.7
	N	79.7
	O	106

^a TATB = C_{6.000}H_{6.050}N_{6.050}O_{6.000}Cl_{0.050} (MW = 260.84) adjusting

C = 6 and assuming that the chlorine found was NH₄Cl.

^b 298 K, H₂O(l) (cal/g).

^c Estimated from total chlorine in TATB.

acid. Elemental analyses for C, H, and N agreed with theory; the mp was 82.0°C. Sample A-530 was not analyzed. The highest density used (1.53 g/cm^3) was chosen so that TNT charges of small diameters would detonate reliably.

Results and Discussion. Results of the basic TNT study, under varying conditions of confinement and density, are presented in Table 43. Column 1 gives the most reliable values for the heat of detonation and products of detonation representative of those found on the CJ isentrope.

The effect of no confinement (columns 1 vs 4 and 5) was much greater than a reduction in density (columns 1 vs 6). The combined effect of lower density and no confinement (column 8) resulted in the lowest ΔH , the maximum CO and H_2 values, and the minimum CO_2 and C(s) values. We noted small differences in ΔH and products between 12.7- and 25.5-mm-diam unconfined charges (column 4) and 6.35-mm-diam unconfined charges (column 5). Products from the smaller charge were reshocked to a lesser degree, which resulted in higher values for ΔH and greater amounts of C(s), CO_2 , and H_2O .

The data in columns 1 and 4 indicate that solid carbon equilibrates rapidly during the reshocking of products that occurs with unconfined charges. The value for solid carbon, frozen out in the initial isentropic expansion, was 3.65 mol/mol of TNT (column 1). If it did not equilibrate, the amount of solid carbon found in the products from unconfined charges (1.01 mol/mol TNT, column 4) should be at least as large as that found in the products from heavily confined charges. The same conclusion can be reached by comparing products from confined and unconfined charges of other explosives below CO_2 balance, e.g., HMX in Table 18.

Table 43 also reports on experiments conducted to find a non-metal replacement for metal confinement for use in the 1.2-m-diam detonation sphere at Site 300. Columns 2 and 3 give the results for alumina and Pyrex; alumina confinement gives a value that is comparable, within experimental error, to gold (column 1) whereas Pyrex (column 2) gives a heat value clearly below that for gold. Although the TNT used in this work was Military Specification, Grade III, the TNT in columns 1, 4, and 5 was a 1966 lot (A-202) whereas the remaining TNT was a later lot (A-530); there may be small differences in the impurity levels.

We were attempting to duplicate the results obtained with gold confinement (column 1) with either Pyrex or alumina confinement. It is clear

Table 43. Heats and products of detonation^a of TNT under varying conditions of confinement and density.^b

Experimental conditions	Confining material							
	1 ^c Gold, detonation	2 Al ₂ O ₃ , detonation	3 Pyrex, detonation	4 ^{d,e} Unconfined, reaction	5 ^{c,d} Unconfined, reaction	6 Gold, detonation	7 NaCl, detonation	8 Unconfined, reaction
Density of confinement, g/cm ³	19.3	3.9	2.32	-	-	19.3	2.13	-
Charge density, g/cm ³	1.533	1.533	1.530	1.53-1.55	1.525	0.998	1.00	1.00
Charge diameter, mm	12.7	12.7	12.7	12.7, 25.4	6.35	12.7	12.7	12.7
Charge weight, g	22	22	22	25	8	15	15	26
-ΔH detonation ^f								
Experimental	1093 ± 11	1070 ± 11	1054 ± 1	632 ± 6	669 ± 8	870 ± 15	896 ± 15	582 ± 15
Calculated from products	1133 ± 15	977 ± 14	949 ± 14	682 ± 22	713 ± 14	877 ± 12	940 ± 12	711 ± 14
Products, mol/mol TNT								
H ₂	1.32	1.30	1.26	1.36	1.54	1.27	1.13	1.31
H ₂ O	1.60	1.37	1.24	0.17	0.28	0.92	1.12	0.37
CO ₂	1.25	1.29	1.31	0.063	0.11	0.77	0.84	0.032
CO	1.98	1.94	1.97	5.89	5.73	3.65	3.49	5.94
C(s) ^g	3.65	3.62	3.57	1.01	1.16	2.31	2.44	0.97
H ₂	0.46	0.42	0.41	2.31	2.28	0.82	0.66	2.25
NH ₃	0.16	0.19	0.21	0.022	0.006	0.20	0.26	0.097
CH ₄	0.099	0.10	0.094	0.0092	0.003	0.19	0.016	0.012
HCM	0.20	0.052	0.058	0.024	0.008	0.071	0.063	0.038
NO	i	0.0013	0.0004	i	i	0.0088	0.033	0.0014
NO ₂	i	0.0013	0.0004	i	i	0.0088	0.033	0.0014
C ₂ H ₆	0.004	0.001	h	h	h	h	h	h
C ₂ H ₂	h	Trace	h	h	h	h	h	h
C ₂ H ₄ O	h	h	h	h	h	h	h	h
C ₃ H ₈	h	0.0005	h	h	h	0.0009	h	h
C ₃ H ₆	h	0.0005	h	h	h	0.0009	h	h
Material recovery, mol%								
C	47.9	48.6	49.3	85.5	83.7	67.3	65.5	86.1
H	100	92.7	87.6	102	103	98.2	102	112
N	94.1	94.8	93.2	92.2	103	94.6	88.6	92.2
O	101	98.3	97.3	102	103	102	106	106

^a Only those experiments that are heavily confined yield heats and products of detonation.

^b One experiment unless otherwise noted. Grade III TNT was used.

^c Studied in 1966-7 using LI Sample #A-202. Remainder studied in 1979 using LI Sample #A-530.

^d Six experiments were conducted, three at each diameter.

^e Two experiments.

^f 298 K, H₂O(l) (cal/g).

^g Determined by difference.

^h Not detected.

ⁱ Not determined.

that with the higher density alumina, the products are subjected to less reshocking than with Pyrex. Column 2 shows larger amounts of C(s) and H_2O and smaller amounts of H_2 than column 3. Of major concern is the large decrease in H_2O when alumina or Pyrex confinement is used. Combining these observations with the lower hydrogen and oxygen recovery obtained with alumina and Pyrex confinement suggests that the finely divided Al_2O_3 and SiO_2 produced on detonation form hydrates.

The work reported in columns 6-8 was conducted primarily for seismic monitoring studies. Comparing columns 6 and 8 shows that for charges at lower densities, the effect of confinement is very evident. We expected that NaCl confinement (column 7) would result in more reshocking of products than gold confinement (column 5) as well as consequent increases in CO and H_2 , decreases in CO_2 , H_2O , C(s), and lower ΔH detonation. However, the opposite effect was observed to a small degree, and the ΔH detonation are essentially the same.

The unusually high hydrogen recovery in column 8 and high oxygen recoveries in columns 7 and 8 cannot be explained. The values in column 8 suggested an error in the water determination, but none could be found in a review of the experimental data. Nitrogen recovery was low for all experiments--the usual observation when solid carbon is a product. The missing nitrogen is contained in the solid carbon in an unidentified manner.

A second study was made on TNT similar to that reported for PETN in Table 34. Computer calculations indicate that the freeze-out temperature of 1500-1800 K occurs at 1-2 relative volumes. As a result of such small expansion, the products from a heavily confined shot should still be contained within the gold cylinder and should not equilibrate with a potentially reactive atmosphere, O_2 or CO_2 , placed within the bomb before detonation.

The results in Table 44 show a large amount of reaction of TNT products in an oxygen atmosphere. The heat of reaction is close to the heat of combustion of TNT, which is reported as 3590 cal/g. As with PETN, we postulate that if a small amount of reaction begins anywhere, it will increase the overall temperature to a point that leads to complete interaction between products and oxygen. The presence of some incompletely oxidized species and absence of free oxygen indicates that insufficient oxygen was present to achieve the CO_2 - H_2O balance desired.

Table 44. Results of detonating heavily confined TNT^a charges in various atmospheres.

Experimental conditions	Atmosphere		
	Vacuum, detonation	Carbon dioxide, detonation	Oxygen, detonation
Balance level attempted	-	CO and H ₂ O	CO ₂ and H ₂ O
Pressure, atm (absolute)	-	1.66	2.46
-ΔH detonation ^c			
Experimental	1093 + 11	1116 + 11	3575 + 35
Calculated from products	1133 + 15	1105 + 15	3594 + 60
Products, mol/mol TNT			
N ₂	1.32	1.22	1.54
H ₂ O	1.60	1.55	2.65
CO ₂	1.25	1.19 ^c	6.82
CO	1.98	2.05	0.38
C(s)	3.65	3.65	Not detected
H ₂	0.46	0.45	0.050
NH ₃	0.16	0.19	0.0050
CH ₄	0.099	0.099	0.0011
HCN	0.020	0.009	0.0005
NO	Not detected	Not detected	0.0011
C ₂ H ₆	0.004	0.003	Not detected
Material recovery, mol%			
C	47.9	48.2	103
H	100	99.9	109
N	94.1	88.1	103
O	101	99.7	101

^a Charge density of TNT = 1.53 g/cm³; charge weight = 25 g.

^b 298 K, H₂O(l) (cal/g).

^c Corrected for CO₂ present in initial CO₂ atmosphere.

The CO₂ atmosphere results were encouraging, yielding ΔH and products very close to those determined in vacuum, a clear indication of little or no interaction of the products after detonation.

Early in our work with the 25-g detonation calorimeter, we conducted another study of TNT on the effects of end confinement that complemented the work done on NM (Table 29; this work is described in the NM experimental section).

We fired heavily confined TNT charges with and without end confinement. Results are presented in Table 45. The experiments having end confinement showed an increase in the heat of detonation and, when the isentropes were

Table 45. Effect of variations in confinement on the heat and products of detonation of heavily confined TNT charges.^a

Experimental conditions		Method of cylindrical confinement		
		Both ends confined, ^b detonation	Non-detonator end confined, ^b detonation	Both ends open, detonation
Number of experiments		1	1	3
-ΔH detonation ^c				
Experimental		1093 + 11	1083 + 11	1032 + 10
Calculated from products		1133 + 15	1116 + 15	1061 + 20
Products, mol/mol TNT				
	N ₂	1.32	1.32	1.33
	H ₂ O	1.60	1.57	1.40
	CO ₂	1.25	1.19	1.06
	CO	1.98	2.13	2.56
	C(s)	3.65	3.57	3.27
	H ₂	0.46	0.52	0.74
	NH ₃	0.162	0.122	0.128
	CH ₄	0.099	0.090	0.076
	HCN	0.020	0.012	0.023
	C ₂ H ₆	0.004	0.002	0.003
Material recovery, mol%				
	C	47.9	48.9	53.2
	H	100	98.6	100
	N	94.1	92.5	93.7
	O	101	101	101

^a Charge density of TNT = 1.53 g/cm³; charge weight = 25 g.

^b End confinement was 0.5-in.-diam by 0.5-in.-long gold plugs.

^c 298 K, H₂O(l) (cal/g).

compared at the same volume, an increase in the species representative of a lower-temperature isentrope (C(s), H₂O, and CO₂), and a corresponding decrease in the species representative of a higher-temperature isentrope (CO and H₂).

XTX-8003

Rationale. XTX-8003 (PETN/Sylgard 182, nominally 80/20 wt%) was studied principally to verify that silicon from Sylgard 182 appeared as SiO₂ in the products, as predicted by computer calculations.

Experimental. XTX-8003 ($C_{1.80}H_{3.64}N_{1.01}O_{3.31}Si_{0.27}$) was pressed in 38.1-mm increments in an evacuated conventional die under 3000 psi pressure and cured in-place at about 85°C for about six hours. The composition determined by analysis was 80.1/19.9 wt% PETN/Sylgard-182.

Results and Discussion. Results are presented in Table 46. The only product found containing silicon was amorphous SiO_2 , which could not be recovered quantitatively. Because the amount of SiO_2 was calculated from the total silicon contained in XTX-8003 and not determined directly, a greater uncertainty was placed on the oxygen recovery. For the detonation experiment, material recoveries were low except that for oxygen. The largest discrepancy, however, was the difference between the observed and calculated ΔH detonation. We attributed this to a combination of low material recovery and uncertainty in the heats of formation of Sylgard-182 and amorphous SiO_2 .

One experiment resulted in an unintentional deflagration. Although not all the explosive was consumed, a reasonably close estimate could be made from an average of the C, H, and N material recovery values. The values in Table 46 are corrected accordingly. Again we note the differences in products and energy between the high-temperature, low-pressure equilibration of a deflagration and the lower-temperature, higher-pressure equilibration of a detonation. For the deflagration, the amounts of CO and H_2 increase, the amounts of H_2O , CO_2 and C(s) decrease, and ΔH reaction decreases.

Table 46. Heat and products of detonation and deflagration of XTX-8003.^a

Experimental conditions		Detonation	Deflagration ^b
Charge weight, g		22	23
Number of experiments		1	1
-ΔH detonation ^c			
experimental		1160 ± 15	1006 ± 15
calculated from products		1490 ± 315	-
Products, mol/mol HE			
	N ₂	0.43	0.47
	H ₂ O	1.01	0.89
	CO ₂	0.41	0.28
	CO	1.07	1.50
	C(s)	0.26	Not detected
	H ₂	0.49	0.86
	NH ₃	0.076	0.004
	CH ₄	0.063	0.019
	HCN	0.0006	0.0009
	SiO ₂ ^d	0.27	0.27
	NO	Not detected	0.078
	C ₂ H ₆	0.002	Not detected
	C ₂ H ₄	Not detected	0.003
Material recovery, mol%			
	C	85.7	94.0
	H	95.7	93.1
	N	92.7	94.6
	O	104	102
	Si	-	-

^a XTX-8003 = PETN/Sylgard 182 (80.1/19.9 wt%) charge density = 1.55 g/cm³ (99.6% TMD), C_{1.80}H_{3.64}N_{1.01}O_{3.31}Si_{0.27} (MW = 100).

^b Not all of XTX-8003 deflagrated. Values are corrected for the amount that reacted based on average material balances for C, H, and N. ΔH was not calculated from the products.

^c 298 K, H₂O(l) (cal/g).

^d Based on total amount of silicon in XTX-8003.

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