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Adiabatic Computation of Internal Blast From Aluminum-Cased Charges in Air

by
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Naval Postgraduate School
Monterey, California
for
Research Department

JANUARY 1982

NAVAL WEAPONS CENTER
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FOREWORD

This report documents the extension of the continuing research effort on internal blast at the Naval Weapons Center to include aluminized fuels in air. Work was performed during fiscal years 1980-1981.

This effort was supported by the Naval Air Systems Command (NAVAIR) and executed by the Naval Weapons Center under the Strike Warfare Weaponry Technology Block Program under Work Request N00019-81-WR-11148, AIRTASK A03W-03P2/008B/1F32-300-000 (appropriation AA1711319). This AIRTASK provides for continued exploratory development in the air superiority and air-to-surface mission areas. Mr. H. B. Benefiel, AIR-350, was the cognizant NAVAIR Technology Administrator. This report was reviewed for technical accuracy by James Weeks.

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(U) Calculations have been carried out, using the HP 9845A desktop computer, for the maximum overpressures developed by combustion of fuels plus aluminum in confined air volumes. In all, eight fuels were chosen, both conventional and explosive. The mass of fuel to that of metal was varied from 0.1 to 10.0 and the total concentration of fuel plus metal ranged from 0.1 to 10.0 kilograms per cubic meter of incident air.

(U) The computations include evaluation of the adiabatic temperatures and of the product compositions, the latter involving the chemical equilibria amongst 28 gaseous and up to five condensed-phase substances.

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INTRODUCTION

Maximum overpressures developed in internal explosions have been the object of study by the Naval Postgraduate School (NPS) for a number of years. Previous reports have appeared on the effects with a variety of C-H-N-O fuels in air¹ and for magnesium alone,² as well as magnesium-fuel mixtures in air.³

The present study represents the extension of this effort to the adiabatic properties of the internal explosions of aluminized fuels in air.

Computations have been carried out using the HP 9845 computer. The expanded capability, relative to the WANG 720C used in the earlier work,¹⁻³ has permitted a much more detailed and precise analysis of this system, in spite of its considerably greater complexity.

Aluminum and fuel are considered to be introduced at 25°C into the air volume at 1 atmosphere. It is assumed that combustion is so rapid that the process can be treated as adiabatic and that the products are distributed uniformly throughout the volume, which is considered constant. The volume of condensed phases is neglected.

The fuels considered are listed in Table 1, along with their chemical formulas and a few pertinent properties. The "relative oxygen content" given in the last column is a rough means of comparing the fuels with one another. It is used as the ordinate in several of the figures.

In all the following, the symbol C will represent the charge, or the mass of fuel, per cubic meter of air and M, the mass of metal (aluminum) per cubic meter of air. Charge-to-metal (C/M) ratios and total concentrations (C + M, in kilograms per cubic meter) were varied over the range 0.1 to 10 for each.

In several of the tables a code has been used to indicate the condensed phases present in the final system. The key to this code is given in Table 2. Again, in most of the figures, the curves have been dotted in those regions where aluminum nitride (AlN) solid is present,

¹ Naval Weapons Center. *Peak Overpressures for Internal Blast*, by G. F. Kinney, R. G. S. Sewell, and K. J. Graham. China Lake, Calif., NWC, June 1979. (NWC TP 6089, publication UNCLASSIFIED.)

² Naval Weapons Center. *Reactive Metals in Internal Explosions: The Combustion of Magnesium in Air*, by R. A. Reinhardt. China Lake, Calif., NWC, February 1978. (NWC TM 3429, publication UNCLASSIFIED.)

³ Naval Weapons Center. *Adiabatic Computation of Internal Blast for Magnesium-Cased Charges in Air*, by R. A. Reinhardt. China Lake, Calif., NWC, April 1979. (NWC TM 3820, GIDEP E202-1481, publication UNCLASSIFIED.)

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TABLE 1. Properties of the Fuels.

Designation	Name and chemical formula	$\Delta U_{f,298}$ (kJ/mole) ^a	Relative oxygen content ^b
PETN	Pentaerythritol tetranitrate $C_5H_8N_4O_{12}$	-489.8	1.33
NC	Nitrocellulose, 13.3% N $C_6H_7N_{2.5}O_{10}$	-812.9	1.05
HMX	<i>sym</i> -Cyclotetramethylenetetra- nitramine, $C_4H_8N_8O_8$	+77.4	1.00
RDX	<i>sym</i> -Cyclotrimethylenetri- nitramine, $C_3H_6N_6O_6$	+111.47	1.00
Pentolite	50% PETN, 50% TNT $C_{6.16}H_{6.25}N_{3.41}O_{8.5}$	-97.9	0.92
Comp B	65% RDX, 35% TNT $C_{1.96}H_{2.53}N_{2.22}O_{2.68}$	+30.7	0.83
TNT	2, 4, 6-Trinitrotoluene $C_7H_5N_3O_6$	-11.75	0.63
C_2H_4O	Ethylene oxide	-47.29	0.25

^aPer mole of formula indicated. Data taken from or computed from the report of footnote 1.

^bNumber of oxygen atoms/(number of carbon atoms plus half the number of hydrogen atoms).

TABLE 2. Code of Condensed Phases in the Aluminum-Fuel-Air System.

Symbol	Formula, name, comments
A	Al_2O_3 , aluminum oxide (alumina) Liquid above 2315 K, solid below 2315 K
N	$AlN(s)$, aluminum nitride Assumed solid whenever produced; melting temperature is unknown.
L	$Al(l)$, liquid aluminum metal
G	$C(s)$, graphite
C	$Al_4C_3(s)$, aluminum carbide Unstable above 2700 K. Below 2700 K, the Gibbs phase rule ⁴ requires that $Al(l)$ and $C(s)$ cannot both be present.

either as the sole condensed phase or along with others. The solid lines represent conditions where liquid or solid aluminum oxide (Al_2O_3) is the only condensed phase present.

⁴ R. A. Alberty and F. Daniels, *Physical Chemistry*, 5th ed. (SI Version). New York, John Wiley & Sons, 1979, pp. 89-91.

BASIS OF CALCULATIONS

From the First Law of Thermodynamics it follows that for an adiabatic, constant-volume, nonflow process there must be no net change in U , the internal energy; or the internal energy of all the products at the adiabatic flame temperature, T , must equal that of the reactants at entering conditions. For each component in the mixture of the products, using the ideal-gas assumption throughout,

$$U_T = U_{298} + \int_{298}^T C_V dt \quad (1)$$

where C_V is the heat capacity at constant volume. For U_{298} the customary thermochemical convention may be chosen of using the internal energy of formation at 298 K. The latter is defined as the internal energy change for the synthesis of the substance considered from the elements in their stable states at the given temperature (298 K). Of the reactant materials, all but the organic fuel are elements in the stable state at 298 K, and thus the initial internal energy is just equal to the internal energy of formation of the fuel, ΔU_f , at 298. Hence, the adiabatic-isochoric condition may be written:

$$\sum_i U_{i,T} = \Delta U_f \quad (2)$$

the index, i , applying to all the product species.

A temperature must be found for which this criterion is met; it may then be identified as the adiabatic flame temperature. The pressure in the system is then calculated from the ideal gas law:

$$P = RT/V \sum n_i \quad (3)$$

in which n_i is the mole number for the i^{th} product component, considering only the gaseous products, V the total volume (1 cubic meter) and R the universal gas constant. The overpressure is found by subtracting 1 bar.

Thermochemical data are represented by a five-parameter expression (of somewhat different form than was used previously³):

$$U_T = B_1 + B_2 T + B_3 T^2 + B_4 \ln T + B_5/T \quad (4)$$

Data were fitted to this equation using a nonlinear regression procedure originally designed by Dr. W. M. Tolles.⁵ Table 3 gives the internal energy parameters for the products

⁵ See L.P. Crawford, "Electron Paramagnetic Resonance of the $\text{CH}_2\text{CO}_2^{\cdot}$ Radical in Irradiated Zinc Acetate Dihydrate," M.S. Thesis, Naval Postgraduate School, Monterey, CA, June 1968, p. 36.

TABLE 3. Internal Energies of Combustion Products.

Expressed as a function of T , the absolute temperature in kilokelvins ($T = T/1000$); values given in joules/mole: $U(T) = B_1 + B_2T + B_3T^2 + B_4 \ln T + B_5/T$

Substance	B1	B2	B3	B4	B5
Al	310931	11660	75	1364	664
AlH	264015	30151	272	-2961	1040
AlOH	-55866	60797	-355	-22628	-4116
Al ₂ O	-149141	50095	-12	-572	1672
Al ⁺	824364	11395	70	2734	2271
Ar	-3718	12473	0	0	0
CO	-84115	31136	-25	-6218	24
CO ₂	-361013	56789	67	-9201	1764
H	213029	12473	0	0	0
OH	166505	34786	-88	-20093	-7842
H ₂	136535	32890	313	-21058	-9413
H ₂ O	50545	63224	-395	-45949	-16417
AlO	844161	86475	-3602	-90479	-39617
AlO ₂	-229458	51802	226	3388	3818
NO	105501	30619	10	-4353	631
N ₂	38785	31651	-61	-7831	-657
O	214445	9604	298	4428	2050
O ₂	32105	29476	662	-6265	-2102
Al(l)	-795	31748	0	0	0
AlN(s)	-297116	37566	181	-407	859
Al ₂ O ₃ (l)	-1632491	136549	0	0	0
Al ₂ O ₃ (s)	-1471366	146423	1833	-37420	-12025
C(s)	-40329	22904	320	3401	5429
CN ⁻	102390	31551	-69	-7172	-392
CN	691554	38828	740	-37192	-24658
C ₂ H	758476	66613	239	-43882	-20692
C ₂ N	538335	54371	-15	-1052	2404
Al ₄ C ₃ (s)	-89327	204334	136	-31427	-2969
HCN	284944	62760	-302	-26216	-5947
HNCO	36816	83592	-474	-28281	-4750
HCO	90276	56166	-353	-19233	-2345
CH ₂ O	54534	85563	-609	-32362	-1612
C ₂ H ₂	474890	92019	-27	-42593	-10539
C ₃	906056	48907	282	-16185	-3220

Substances are gaseous unless otherwise specified.

considered; data from the JANAF Tables⁶ were used as the primary source. For the aluminum species below 2767 K (the normal boiling point of the metal) the thermochemical data were first recomputed to accommodate the universal choice of aluminum vapor as the reference state. (See Appendix A for further discussion of this point.)

⁶ National Bureau of Standards, *JANAF Thermochemical Tables*, 2nd ed., by D. R. Stull and H. Prophet. Washington, D.C., NBS, June 1971.

EQUILIBRIUM CONSIDERATIONS

SPECIES CONSIDERED

The equilibrium-stoichiometric calculations involved the consideration of 28 gaseous species and up to five condensed phases. The gaseous species are, rather arbitrarily, divided into "major" and "minor" categories:

Major (gaseous): Al, Al₂O, Ar, CO, CO₂, H₂, H₂O, N₂, O₂

Minor (gaseous): AlH, AlOH, Al⁺, H, OH, AlO, AlO₂, NO, O, CN⁻, CN, C₂H, C₂N, HCN, HNC, CH₂O, C₂H₂, C₃

Condensed: Al(l), Al₂O₃ (l or s), AlN(s), Al₄C₃(s), C (graphite).

Using the computational scheme described below, in an abbreviated version, the following species were eliminated as never reaching an appreciable amount under any of the conditions to be anticipated: AlHO, AlHO₂, Al₂O₂, C(g), C₂, C₂O, C₃O₂.

Ion formation was also looked for in the same way. It was realized at once that simple equilibrium ionization to produce appreciable electron concentrations would not occur, even at 4500 K (the highest computed temperature). But ions might be formed in pairs by the exchange of an electron between neutral species. It was concluded, in this preliminary screening, that there was the possibility of producing Al⁺ and CN⁻ at high temperatures and under ideal stoichiometries.

A comment should be made regarding the vaporization of the condensed phases. At the temperatures considered, liquid aluminum is fairly volatile, and aluminum vapor is thus considered as one of the important species. The vapor pressures of AlN(s) to AlN(g) or of C(s) to either C(g) or C₂(g) are too small to be of significance; C₃(g) was included in the scheme, though no system was found in which an appreciable amount occurred. Al₄C₃ is unstable, relative to the elements, above 2700 K. As far as is known, Al₂O₃ does not exist as such in the vapor phase; rather, Al₂O₃ undergoes equilibrium dissociation at high temperatures into a complex mixture including Al₂O, AlO, O, etc.

EQUILIBRIUM DATA

For each species there exists at every temperature the equilibrium constant of formation; *i.e.*, the equilibrium constant for the synthesis of 1 mole from the elements in their standard states. Standard states chosen for this purpose are: Al(g), C(s), H₂(g), N₂(g), O₂(g). Data were taken from the JANAF Tables⁶ and fitted to the equation

$$\log_{10}K = A_1 + A_2/(A_3 + T) + A_4T \quad (5)$$

using the nonlinear regression scheme.⁵ For aluminum compounds below 2700 K, which is the boiling point of the metal, the JANAF data must first be recalculated to account for the change in standard state from liquid metal used in the tables to the vapor as used by us. Table 4 gives the parameters for the equilibrium-constant equation (Equation 5).

In application, the formation constants must also be converted from K (that is, in terms of pressures) to K_n (in terms of mole numbers). At the beginning of any computation at a new temperature, this conversion is carried out from the relation

$$K_p = K_n (V/RT)^{\Delta n} \quad (6)$$

where Δn is the change in number of moles of gas for the synthesis reaction. Then for any species the mole number is given as a known function of the K_n of formation of the mole numbers of Al, H₂, N₂ and O₂, and of the activity of carbon (standard state, graphite). The activity concept is discussed in Appendix A.

TABLE 4. Equilibrium Constants of Formation of Combustion Products.

Logarithm (base 10) of the formation constant of the indicated substance, expressed as a function of T , the absolute temperature in kilokelvins ($T = T/1000$): $\text{LOG}(10) K = A1 + A2/(A3 + T) + A4T$.

Substance	A1	A2	A3	A4
AlH	-2.046	3.096	-0.061	-0.076
AlOH	-6.828	26.915	0.002	0.010
Al ₂ O	-8.582	40.171	-0.009	-0.175
Al ⁺	2.255	-32.796	0.027	0.098
CO	4.593	6.108	0.030	-0.067
CO ₂	0.087	20.642	0.001	-0.024
H	3.132	-12.016	0.019	0.015
OH	0.769	-1.969	-0.016	-0.015
H ₂ O	-3.056	13.305	0.014	-0.005
AlO	-2.943	12.989	0.005	0.068
AlO ₂	-6.148	26.186	-0.007	0.010
NO	0.710	-4.870	0.008	-0.009
O	3.497	-13.459	0.010	0.006
Al(l)	-5.953	15.658	-0.021	0.090
AlN(s)	-10.936	31.054	-0.037	-0.117
Al ₂ O ₃ (l)	-40.607	154.393	0.282	1.928
Al ₂ O ₃ (s)	-29.436	118.807	-0.006	0.506
CN	0.826	0.005	-2.418	0.047
CN	5.092	-22.218	-0.012	-0.016
C ₂ H	6.529	-24.269	-0.012	-0.043
C ₂ N	7.060	-29.343	0.000	-0.066
Al ₄ C ₃ (s)	-24.903	71.143	-0.049	-0.519
HCN	1.607	-6.807	-0.012	-0.008
HNCO	-25.740	96.491	2.563	2.862
HCO	2.221	1.209	0.219	-0.060
CH ₂ O	-2.036	6.770	0.018	-0.016
C ₂ H ₂	2.655	-11.332	-0.016	0.000
C ₂	10.850	-41.395	-0.016	-0.186

Substances are gaseous unless otherwise specified.

EQUILIBRIUM CALCULATIONS

For argon the mole number is always 0.4036, the number of moles in 1 cubic meter of standard air at 298 K, 1 bar. For each of the remaining five elements a material balance equation may be written, representing the conservation of the number of atoms of the element. Each mole number is a function of those of the elements in standard states and of the activity of carbon; hence five simultaneous nonlinear equations in five unknowns are obtained.

The number of simultaneous equations that must be considered is reduced whenever a condensed phase is present, since each condensed phase introduces a new restriction. It has been found that, in all cases which are terminal states for an adiabatic process of the type considered, there is at least one condensed phase (most commonly Al_2O_3) and sometimes more, up to as many as four in one case. In brief, then it becomes necessary to solve a system of from two to four simultaneous nonlinear equations. For this purpose the Newton-Raphson method was used, as outlined in Appendix B.

Initial approximations for entering the computational scheme are obtained by first assuming that liquid aluminum plus condensed Al_2O_3 are present, from which case fairly simple iterations, based on chemical stoichiometric considerations, lead to solutions to the equations without requiring the formal Newton's method calculations. Tests are then made for the actual presence of these two phases: If both are present, the calculation stands; if either is absent, the Newton's method is initiated, using as initial approximations those mole numbers found from this first calculation. Typically, three to six iterations are made in each use of Newton's method. Further detail on the computational scheme is intended for a forthcoming report.

RESULTS

For all the systems studied, a large number of properties at the adiabatic condition were found. These include adiabatic temperature and overpressure (which are reported for each case) and product yields, heat capacity, and isentropic coefficient (some representative values of which are reported). Total concentration (metal plus fuel) was varied regularly over the range 0.10 to 10.0 kg/m^3 . For the metal-fuel-air systems C/M was varied systematically also from 0.10 to 10.0.

Table 2 gave the key to the condensed phases present, as used throughout Tables 5 through 7. In Table 5 are given overpressures (bars), adiabatic temperatures (K), and product yields in mole % for "pure" aluminum in air.* In Table 6 adiabatic temperature and overpressure are given for each of the eight chosen fuels in air, but in the absence of metal.**

* Because of limitations in the structure of the computer program, these calculations had to be run for Al + 0.01% C. This trace of carbon is quite trivial to the computed results.

** For this purpose a simplified program was used, constructed with the aid of Kenneth J. Graham, Naval Weapons Center, in which all reference to aluminum was omitted.

**TABLE 5. Combustion of Pure Aluminum in Air:
Adiabatic Temperature, Overpressure, and Product Yields.**

Concentration, kg/m ³	Temperature, K	Over- pressure, bars	Partial pressure, bars ^a								Product yields, number of moles		
			Al	Al ₂ O	AlO	AlO ₂	NO	N ₂	O ₂	O	Al(l)	Al ₂ O ₃ (l)	AlN(s)
0.1	2623	7.2	0	0	0	0	0.20	6.76	1.13	0	—	1.85	—
0.2	3813	10.5	0.01	0.01	0.04	0.03	0.50	9.73	0.37	0.63	—	3.56	—
0.4	4034	11.6	0.53	0.66	0.30	0.03	0.16	10.47	0.26	0.03	—	4.16	—
1.0	2987	9.9	0.54	3.24	0	0	0	7.05	0	0	—	1.29	6.17
2.0	3158	10.8	2.86	4.45	0	0	0	4.41	0	0	—	—	29.4
4.0	3104	8.4	3.98	4.37	0	0	0	0.96	0	0	4.34	—	55.6
10.0	2223	-0.4	0.04	0.48	0	0	0	0	0	0	2.93	4.8 ^b	63.0

^aTo the nearest 0.01 bar. Balance is argon.

^bSolid Al₂O₃.

**TABLE 6. Combustion of Pure Fuels in Air: Overpressures
(With Adiabatic Temperatures in Parentheses).**

Concentration, kg/m ³	C ₂ H ₄ O	TNT	Comp B	Pentolite	RDX	HMX	NC	PETN
0.1	7.8 (2408)	4.8 (1625)	3.8 (1335)	4.0 (1384)	3.3 (1170)	3.2 (1149)	3.1 (1137)	2.8 (1053)
0.2	10.8 (2813)	8.2 (2437)	6.8 (2022)	7.0 (2095)	5.9 (1762)	5.8 (1729)	5.6 (1706)	5.1 (1574)
0.4	11.9 (2275)	12.2 (2972)	11.3 (2755)	11.3 (2805)	10.3 (2501)	10.1 (2460)	9.5 (2419)	9.0 (2258)
1.0	13.7 (1513) (G)	19.5 (3038)	20.0 (3214)	19.8 (3236)	19.3 (3129)	19.0 (3095)	17.0 (2935)	17.2 (2944)
2.0	20.2 (1399) (G)	29.3 (2821)	33.1 (3363)	32.7 (3396)	32.7 (3376)	32.2 (3336)	27.2 (3018)	28.9 (3209)
4.0	34.3 (1369) (G)	48.0 (2617)	58.9 (3437)	58.2 (3493)	59.3 (3546)	58.1 (3496)	46.3 (2991)	51.8 (3392)
10.0	78.3 (1393) (G) ^a	103.1 (2559) (G)	136.4 (3499)	135.0 (3582)	140.0 (3715)	136.8 (3651)	102.6 (2929)	121.5 (3578)

^a(G) indicates solid carbon is present.

Table 7 gives overpressure in bars, with the temperature in parentheses for the aluminum-fuel-air mixtures. Each portion of the table is devoted to a particular fuel and the fuels are arranged from the most oxygen-deficient, ethylene oxide, to the most oxygen-rich, PETN. In all the following, C refers to the concentration of fuel ("charge") and M to that of metal, in kilograms per cubic meter. C/M thus represents the charge-to-metal ratio and C + M the total concentration, in kilograms per cubic meter. Again for each table entry is a code indicating the condensed phase or phases present as indicated in Table 2.

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TABLE 7. Overpressure, in bars, Adiabatic Temperature, in Kelvins (in parentheses) and Condensed Phases for the Combustion of Aluminized Fuels.^a

Fuel: Ethylene oxide							
C+M	C/M						
	0.1	0.25	0.5	1	2	4	10
0.1	7.2 (2592) A	7.3 (2563) A	7.4 (2534) A	7.5 (2499) A	7.6 (2467) A	7.7 (2443) A	7.7 (2425) A
0.2	10.5 (3661) A	10.5 (3516) A	10.6 (3378) A	10.7 (3241) A	10.8 (3116) A	10.9 (3011) A	10.9 (2913) A
0.4	12.2 (3936) A	12.9 (3825) A	13.6 (3700) A	14.3 (3518) A	14.3 (3216) A	13.7 (2885) A	12.8 (2574) A
1.0	11.3 (2968) AN	12.9 (2943) AN	14.7 (2907) AN	17.0 (2836) AN	18.5 (2656) AN	16.8 (2155) NG	16.3 (1934) ANG
2.0	13.6 (3137) N	17.0 (3117) N	20.8 (3077) N	24.6 (2955) N	26.7 (2611) NG	25.5 (2118) NG	26.2 (1991) ANG
4.0	13.9 (3052) NL	20.2 (2982) NLG	28.6 (2949) NLG	37.9 (2891) NG	44.6 (2646) NG	43.4 (2133) ANG	45.6 (2045) AG
10.0	12.2 (2460) ALNC	29.4 (2570) ALNC	50.6 (2640) ALNGC	72.2 (2663) ALNGC	94.6 (2670) ANG	103.3 (2367) ANG	103.2 (2032) AG
Fuel: TNT							
0.1	7.0 (2536) A	6.8 (2432) A	6.6 (2315) A	6.4 (2210) A	5.9 (2020) A	5.5 (1869) A	5.1 (1739) A
0.2	10.3 (3666) A	10.1 (3479) A	9.8 (3276) A	9.4 (3062) A	9.1 (2865) A	8.8 (2703) A	8.5 (2565) A
0.4	12.0 (4029) A	12.5 (4009) A	13.0 (3962) A	13.2 (3791) A	12.9 (3480) A	12.6 (3258) A	12.3 (3092) A
1.0	10.9 (2980) AN	12.0 (2972) AN	13.4 (2960) AN	16.4 (3283) A	19.4 (3567) A	20.8 (3589) A	20.3 (3320) A

^aSee Table 2 for condensed phases code.

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TABLE 7. Overpressure, in bars, Adiabatic Temperature, in Kelvins (in parentheses) and Condensed Phases for the Combustion of Aluminized Fuels^a (Contd.).

Fuel: TNT							
C+M	C/M						
	0.1	0.25	0.5	1	2	4	10
2.0	12.7 (3136) N	15.0 (3102) N	17.6 (3043) N	20.9 (2980) AN	24.2 (2948) AN	26.7 (2906) AN	30.7 (3126) A
4.0	13.5 (3154) NL	19.7 (3196) NL	26.4 (3220) N	33.6 (3190) N	40.4 (3118) N	45.1 (3015) N	47.4 (2857) N
10.0	9.1 (2529) ALNC	22.3 (2829) NLG	40.7 (3090) NLG	65.3 (3235) NLG	85.5 (3234) N	98.3 (3137) N	104.4 (2909) NG
Fuel: Composition B							
0.1	7.0 (2515) A	6.7 (2385) A	6.6 (2315) A	6.0 (2086) A	5.4 (1844) A	4.8 (1650) A	4.3 (1482) A
0.2	10.3 (3651) A	10.0 (3444) A	9.6 (3213) A	9.1 (2952) A	8.6 (2686) A	8.0 (2442) A	7.5 (2243) A
0.4	12.0 (4042) A	12.5 (4032) A	13.0 (3976) A	13.0 (3738) A	12.5 (3390) A	12.1 (3139) A	11.6 (2930) A
1.0	11.0 (2985) AN	12.3 (2982) AN	15.5 (3494) A	18.7 (3867) A	20.8 (3925) A	20.9 (3695) A	20.4 (3424) A
2.0	12.8 (3114) N	15.1 (3028) AN	18.4 (3029) AN	22.6 (3081) A	30.4 (3768) A	33.9 (3878) A	33.9 (3629) A
4.0	14.8 (3183) NL	21.6 (3227) N	27.8 (3173) N	35.4 (3093) AN	46.2 (3345) A	57.5 (3842) A	59.9 (3750) A
10.0	11.1 (2613) ALN	29.3 (3104) NL	52.6 (3285) NL	76.2 (3255) N	96.9 (3212) AN	125.2 (3715) A	140.2 (3858) A
Fuel: Pentolite							
0.1	7.0 (2518) A	6.7 (2393) A	6.6 (2315) A	6.1 (2106) A	5.4 (1873) A	4.9 (1686) A	4.4 (1524) A

^aSee Table 2 for condensed phases code.

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**TABLE 7. Overpressure, in bars, Adiabatic Temperature, in Kelvins
(in parentheses) and Condensed Phases for the
Combustion of Aluminized Fuels^a (Contd.).**

Fuel: Pentolite							
C+M	C/M						
	0.1	0.25	0.5	1	2	4	10
0.2	10.3 (3651) A	9.9 (3445) A	9.6 (3218) A	9.1 (2968) A	8.6 (2716) A	8.1 (2489) A	7.6 (2304) A
0.4	12.0 (4045) A	12.5 (4037) A	12.9 (3979) A	12.9 (3735) A	12.4 (3394) A	12.0 (3156) A	11.6 (2962) A
1.0	11.0 (2984) AN	12.3 (2981) AN	15.7 (3570) A	18.7 (3918) A	20.6 (3946) A	20.6 (3698) A	20.2 (3434) A
2.0	12.8 (3108) N	15.1 (3025) AN	18.3 (3025) AN	23.5 (3268) A	30.6 (3873) A	33.5 (3918) A	33.4 (3649) A
4.0	14.6 (3166) NL	21.4 (3205) N	27.4 (3138) N	35.1 (3084) AN	47.9 (3573) A	57.6 (3957) A	58.9 (3793) A
10.0	10.4 (2568) ALN	27.7 (2953) NL	50.7 (3193) NL	74.3 (3178) AN	95.8 (3197) AN	127.9 (3929) A	138.4 (3934) A
Fuel: RDX							
0.1	6.9 (2504) A	6.6 (2360) A	6.5 (2272) A	5.8 (2016) A	5.1 (1745) A	4.4 (1527) A	3.8 (1336) A
0.2	10.2 (3643) A	9.9 (3424) A	9.5 (3175) A	8.9 (2881) A	8.2 (2564) A	7.6 (2311) A	6.7 (2024) A
0.4	12.0 (4049) A	12.5 (4042) A	13.0 (3976) A	12.9 (3700) A	12.2 (3322) A	11.7 (3031) A	10.9 (2758) A
1.0	11.1 (2987) AN	12.9 (3141) A	16.4 (3734) A	19.2 (4008) A	20.8 (3962) A	20.5 (3661) A	19.9 (3369) A
2.0	12.9 (3100) N	15.4 (3037) AN	18.9 (3043) AN	26.2 (3672) A	32.0 (4051) A	34.0 (3955) A	33.5 (3646) A

^aSee Table 2 for condensed phases code.

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**TABLE 7. Overpressure, in bars, Adiabatic Temperature, in Kelvins
(in parentheses) and Condensed Phases for the
Combustion of Aluminized Fuels^a (Contd.).**

Fuel: RDX							
C+M	C/M						
	0.1	0.25	0.5	1	2	4	10
4.0	15.5 (3197) NL	22.1 (3217) N	28.2 (3108) AN	37.0 (3123) AN	53.1 (3993) A	60.0 (4119) A	59.9 (3843) A
10.0	12.4 (2745) NL	33.2 (3189) NL	57.8 (3328) N	79.6 (3253) AN	115.2 (3904) A	138.0 (4272) A	142.6 (4052) A
Fuel: HMX							
0.1	6.9 (2502) A	6.6 (2356) A	6.5 (2266) A	5.8 (2007) A	5.0 (1732) A	4.3 (1511) A	3.7 (1318) A
0.2	10.2 (3641) A	9.9 (3420) A	9.5 (3168) A	8.9 (2870) A	8.1 (2547) A	7.5 (2288) A	6.6 (1995) A
0.4	12.0 (4049) A	12.5 (4041) A	12.9 (3973) A	12.8 (3689) A	12.2 (3306) A	11.6 (3010) A	10.8 (2728) A
1.0	11.1 (2987) AN	12.8 (3124) A	16.3 (31720) A	19.1 (3999) A	20.6 (3948) A	20.3 (3637) A	19.7 (3340) A
2.0	12.9 (3099) N	15.3 (3036) AN	18.7 (3041) AN	25.9 (3641) A	31.7 (4033) A	33.6 (3929) A	33.0 (3610) A
4.0	15.4 (3196) NL	21.9 (3214) N	28.0 (3106) AN	36.7 (3120) AN	52.4 (3961) A	59.2 (4091) A	58.9 (3800) A
10.0	12.3 (2733) NL	26.9 (2985) NL	46.5 (3151) NL	78.8 (3249) AN	113.1 (3850) A	136.0 (4235) A	139.8 (3997) A
Fuel: Nitrocellulose							
0.1	6.9 (2501) A	6.6 (2354) A	6.4 (2261) A	5.7 (2001) A	4.9 (1724) A	4.3 (1501) A	3.6 (1308) A
0.2	10.2 (3630) A	9.8 (3400) A	9.3 (3144) A	8.7 (2848) A	7.9 (2528) A	7.3 (2270) A	6.4 (1974) A

^aSee Table 2 for condensed phases code.

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TABLE 7. Overpressure, in bars, Adiabatic Temperature, in Kelvins
(in parentheses) and Condensed Phases for the
Combustion of Aluminized Fuels^a (Contd.).

Fuel: Nitrocellulose							
C+M	C/M						
	0.1	0.25	0.5	1	2	4	10
0.4	12.0 (4044) A	12.4 (4030) A	12.7 (3944) A	12.3 (3609) A	11.6 (3226) A	11.0 (2944) A	10.2 (2679) A
1.0	10.9 (2983) AN	12.2 (3010) A	15.5 (3623) A	18.1 (3932) A	19.1 (3816) A	18.3 (3449) A	17.6 (3163) A
2.0	12.5 (3077) N	14.7 (3020) AN	17.7 (3018) AN	23.3 (3416) A	28.9 (3897) A	29.5 (3672) A	28.3 (3309) A
4.0	14.5 (3148) NL	20.4 (3150) N	25.8 (3062) AN	33.4 (3068) AN	46.2 (3718) A	51.2 (3801) A	48.7 (3376) A
10.0	9.8 (2569) ALN	26.1 (2760) ALN	48.1 (3021) NL	69.8 (3153) AN	94.6 (3436) A	115.9 (3899) A	111.4 (3424) A
Fuel: PETN							
0.1	6.9 (2495) A	6.6 (2342) A	6.4 (2241) A	5.6 (1967) A	4.8 (1675) A	4.1 (1440) A	3.4 (1234) A
0.2	10.2 (3630) A	9.8 (3397) A	9.3 (3133) A	8.6 (2817) A	7.8 (2467) A	7.0 (2182) A	6.1 (1863) A
0.4	12.0 (4058) A	12.4 (4052) A	12.7 (3962) A	12.3 (3618) A	11.6 (3219) A	10.9 (2902) A	10.0 (2580) A
1.0	11.1 (2987) AN	13.6 (3401) A	16.6 (3920) A	18.8 (4098) A	19.5 (3895) A	18.8 (3521) A	18.0 (3215) A
2.0	12.7 (3066) N	15.3 (3036) AN	18.9 (3089) A	26.8 (4028) A	30.6 (4162) A	30.8 (3844) A	29.8 (3493) A
4.0	15.5 (3172) NL	21.4 (3144) N	27.9 (3103) AN	41.4 (3803) A	51.9 (4290) A	54.4 (4090) A	52.8 (3701) A

^aSee Table 2 for condensed phases code.

TABLE 7. Overpressure, in bars, Adiabatic Temperature, in Kelvins (in parentheses) and Condensed Phases for the Combustion of Aluminized Fuels^a (Contd.).

Fuel: PETN							
C+M	C/M						
	0.1	0.25	0.5	1	2	4	10
10.0	11.8 (2656) ALN	32.4 (3016) NL	55.1 (3171) AN	81.8 (3464) A	116.4 (4443) A	126.3 (4353) A	124.6 (3929) A

^aSee Table 2 for condensed phases code.

In Table 8 is given the set of product yields for the TNT-aluminum-air system at C/M = 1.0, chosen as representative. Mole % in the vapor is given for all components that reach at least 0.1% at some point. Numbers of moles of condensed phases are also provided. Also given are C_V , the specific heat capacity at constant volume, in kJ/kg/K and an isentropic parameter λ , defined such that $TV^{\lambda-1}$ is constant for an isentropic process of small displacement. Computation and significance of C_V and λ are discussed in Appendix C. It should be added that product-yield data and values of C_V and λ are available for all the systems run but have not been included in this report due to the bulk of data involved.

DISCUSSION

PURE ALUMINUM IN AIR

Table 5, as remarked, gives the data for aluminum-air mixtures. It is noted that temperature vs concentration shows a maximum at 0.4 kg/m³. This corresponds reasonably well with the notion that at 0.305 kg/m³, aluminum and oxygen are present in stoichiometrically equivalent amounts to form Al₂O₃. Beyond this point, to an increasing extent, Al₂O₃(l) is being converted to Al₂O(g) by the *endothermic* (energy-absorbing) reaction



The drop in temperature is arrested when aluminum nitride begins to form. This exothermic process,



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TABLE 8. Combustion of TNT-Aluminum in Air at C/M = 1.0: Temperature, Pressure, Product Yield and Isentropic Parameters.

		C + M, kg/m ³						
		0.1	0.2	0.4	1.0	2.0	4.0	10
T, K		2210	3062	3791	3283	2980	3190	3235
Overpressure, bars		6.4	9.5	13.2	16.4	30.1	33.6	65.3
Mole % in the gas ^a	Al	—	—	0.1	2.4	2.2	8.9	9.4
	AlH	—	—	—	0.1	0.2	1.0	1.5
	AlOH	—	—	—	0.1	0.1	0	0
	Al ₂ O	—	—	0.1	8.4	12.7	8.1	8.4
	CO	—	2.4	12.2	24.1	34.8	45.4	52.0
	CO ₂	3.8	5.1	1.5	0.1	0	0	0
	H	—	0.2	3.1	2.3	1.1	1.8	1.6
	OH	0.1	1.1	1.7	0	0	0	0
	H ₂	—	0.1	1.2	7.2	11.7	14.6	17.0
	H ₂ O	1.3	1.9	1.2	0.1	—	—	—
	AlO	—	—	0.3	0.1	—	—	—
	AlO ₂	—	—	0.1	—	—	—	—
	NO	1.1	3.1	2.2	—	—	—	—
	N ₂	78.4	76.8	71.5	54.5	36.6	18.2	4.6
	O	0	1.1	2.7	—	—	—	—
	O ₂	14.1	7.2	1.1	—	—	—	—
HCN	—	—	—	—	0.1	1.4	2.6	
C ₂ H ₂	—	—	—	—	—	0.2	2.3	
Moles of AlN(s)	—	—	—	—	11.6	40.0	99.7 ^b	
Moles of Al ₂ O ₃ (l)	0.9 ^c	1.9	3.5	3.1	0.4	—	—	
C _v , J/K/g	1.18	2.12	3.72	1.69	25.8	12.2	10.3	
λ ^d	1.23	1.14	1.10	1.17	1.07	1.07	1.06	

^aBalance is argon.

^bPlus 17.2 moles Al(l) and 6.0 moles C(s).

^cSolid Al₂O₃.

^dThe isentropic coefficient defined in Appendix C.

is not possible until the free oxygen has been consumed in the formation of aluminum oxide. The final drop in temperature at the high-concentration end is the result of the appearance of liquid aluminum metal in large quantities, which serves as an energy sink due solely to its heat capacity.

The curve of total pressure vs concentration, as shown subsequently, is labeled "C/M = 0." At low concentrations the pressures reflect the corresponding temperature

effects, but beyond the equivalence point (0.3 kg/m^3) the pressure does not change as much as the temperatures might suggest, largely a result of the increased number of moles of gaseous Al_2O . At the high-concentration extreme the surprising circumstance is noted that the total pressure drops to less than atmospheric (resulting in a negative overpressure). At this point only about 1% of the material present is in the gas phase.

TEMPERATURE AND PRESSURE IN ALUMINUM-FUEL-AIR MIXTURES*

Figure 1 shows temperature vs total concentration ($C + M$) for two representative C/M ratios for TNT (an oxygen-deficient explosive) and PETN (an oxygen-rich explosive). For the most part, the maximum in temperature occurs fairly close to the equivalence point for the formation of $\text{Al}_2\text{O}_3 + \text{CO} + \text{H}_2 + \text{N}_2$ (marked E on the curves) and for approximately the same reason as with aluminum itself. But for PETN of low aluminum content—large C/M (and the same is observed for other oxygen-rich fuels)—no maximum is observed even though the systems become oxygen-deficient at high concentrations. There is sufficient oxygen in the fuel so that as $C + M$ increases the principal effect is the exothermic production of Al_2O from its elements. This results in a slowing of the temperature rise, since the process is less exothermic than the formation of Al_2O_3 , but sufficient so as to overcome the energy-wasting production of H_2 . The lower right-hand part of the figure, shown by dotted lines, is that where AlN is present.

The pronounced dependence of total pressure on total concentration is shown in Figure 2, for TNT at two different C/M ratios. These curves are explainable on the basis

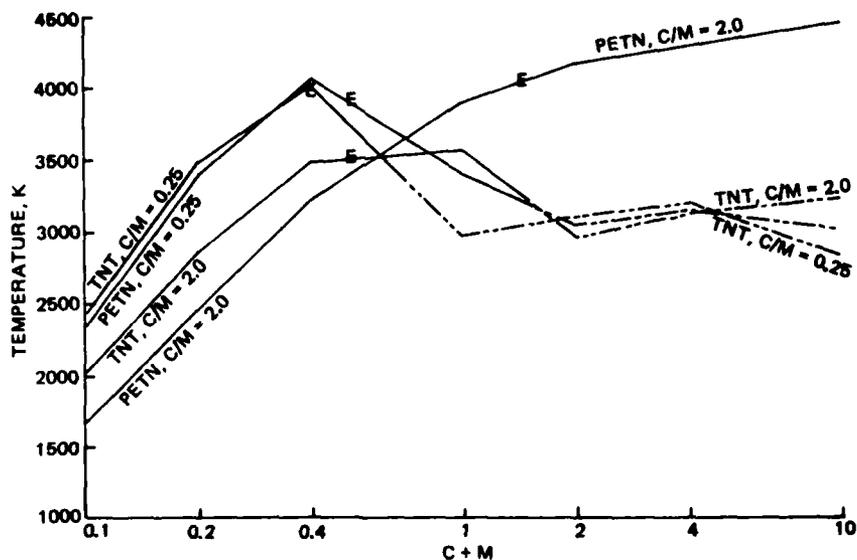


FIGURE 1. Adiabatic Temperature vs Total Concentration for TNT and PETN With Aluminum and Air.

* Note that in Figures 1 through 5, dotted lines are used to indicate the presence of AlN solid.

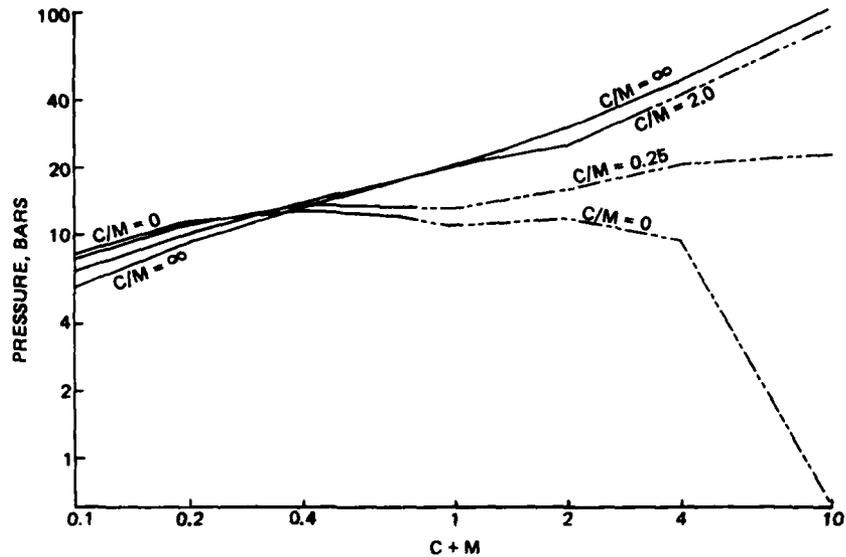


FIGURE 2. Total Pressure vs Total Concentration of Pure TNT, Pure Aluminum and TNT-Aluminum Mixtures in Air.

of the temperature effects just discussed, taking into account the increased production of gaseous products (CO , H_2 , and Al_2O) at higher concentrations. Table 8 shows this effect, especially if one multiplies the mole %s by the total mole numbers. It is interesting to note, by comparison with the temperature effects in Figure 1, that at high concentration the overpressure continues to rise rapidly at $C/M = 2$ but not for $C/M = 0.25$, even though the temperatures behave similarly in this region (where AlN is the condensed phase present). For comparison purposes the curves for pure TNT ($C/M = \infty$) and also for pure Al ($C/M = 0$) which was discussed earlier are included in the figure.

The effects of C/M ratio on temperature and overpressure are shown in Figure 3 for PETN at two different total concentrations. Curves for other fuels will differ only in details. The decrease in temperature as C/M increases at low concentration ($C + M = 0.2 \text{ kg/m}^3$) is characteristic of the oxygen-rich regime. Aluminum has a higher heating value (ca 31 kJ/g) than any of the fuels considered here; thus, replacing aluminum by fuel, as C/M is increased, would result in a lowering of temperature. (A hydrocarbon, however, would have shown the reverse trend.) At the higher concentration the mixture is oxygen-deficient for small values of C/M ; increasing the content of PETN (or other explosive fuel) improves the oxygen balance and the temperature is seen to rise to a maximum; this maximum in many cases, but not all, corresponds closely to the equivalence point ($\text{Al}_2\text{O}_3 + \text{CO}$). The pressure effects seen in Figure 3 parallel at least qualitatively those of temperature, though the pressure maximum at $C + M = 2.0 \text{ kg/m}^3$ is very shallow.

The effect of different fuels is given for a variety of total concentrations, all at $C/M = 1.0$, for the temperature in Figure 4 and for overpressure in Figure 5. The ordinate for these plots is the *relative oxygen content* (ROC) defined previously³ as the number of oxygen

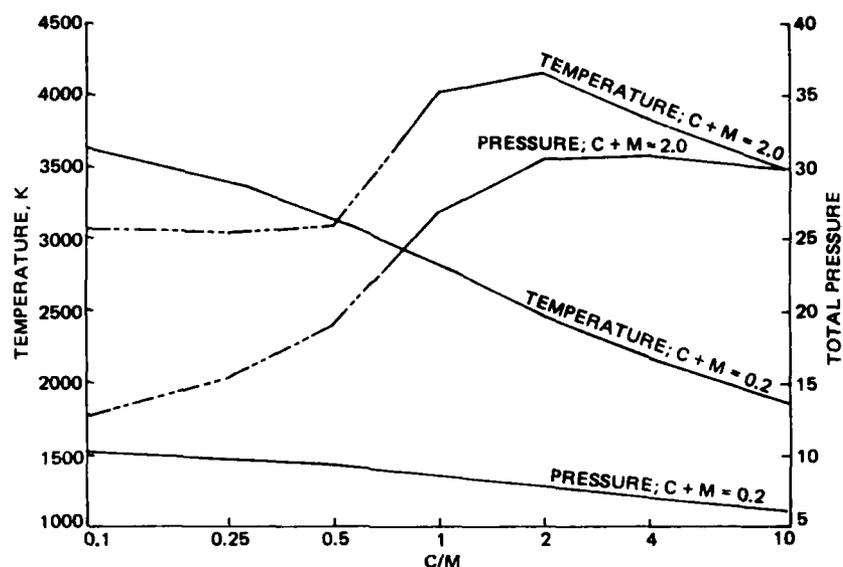


FIGURE 3. Adiabatic Temperature and Total Pressure vs Charge- to-Metal Ratio for PETN With Aluminum and Air.

atoms divided by the sum of the number of carbon atoms plus half the number of hydrogen atoms. $ROC = 1.0$ corresponds to a material just balanced for the formation of $CO + H_2O$. The complex appearance of the temperature plots of Figure 4 is in part explainable. At low concentration ($C + M = 0.2 \text{ kg/m}^3$) all the systems are oxygen-rich. The additional oxygen supplied by the fuels of higher ROC is thus a liability; which is to say that the heating value per unit mass decreases as the oxygen content increases. Even at $C + M = 0.4 \text{ kg/m}^3$ the C_2H_4O -Al-air system is somewhat oxygen-deficient, resulting in the drop in temperature from TNT to ethylene oxide along this curve. At the higher concentrations the systems are mostly oxygen-deficient, and increasing the oxygen content alleviates this somewhat, resulting in generally increasing temperature with ROC. The irregularity between nitrocellulose and RDX (HMX is virtually identical in behavior to RDX) is presumably the result of the positive energy of formation of RDX (111 kJ/mole) contrasted to the considerable negative energy of formation of nitrocellulose (-813 kJ/mole).

The pressure effects, in Figure 5, are much less striking, albeit parallel. In particular can be noted the lowered pressure for oxygen-rich fuels at low concentration and the enhanced pressure for PETN, relative to all the others, at high concentration.

CONDENSED PHASES

It is quite evident, from an examination of the tables and figures, that the nature of the condensed phases present can make profound alterations in the way in which adiabatic temperature and overpressure vary with concentration or C/M ratio. For this reason it is of

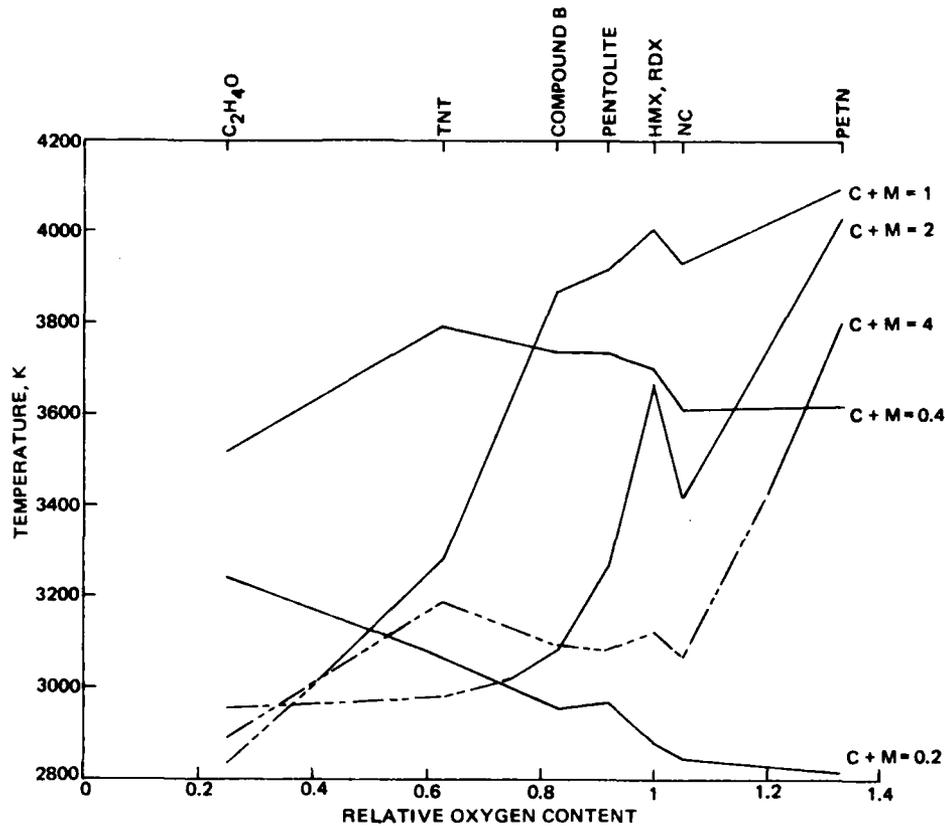


FIGURE 4. Adiabatic Temperature vs Relative Oxygen Content for Combustion of Eight Fuels in the Presence of Aluminum and Air.

considerable interest to observe which phases are present under various conditions and to attempt to consider how temperature and pressure might thereby be affected.

In Figure 6 is shown approximately the regions where various condensed phases exist under adiabatic conditions for the TNT-aluminum-air system.* Other fuels will resemble TNT qualitatively, but the regions will be skewed at high C/M values according to the oxygen content. For example, AlN is restricted to the lower right-hand 20% of the diagram for PETN.

It may be considered that, as C + M is increased, the effect is that of adding the elements as Al(l), C(s), H₂, N₂, and O₂; any oxygen-deficiency will be enhanced as C + M is increased, thus making it easier for AlN to be formed. Exothermic processes will tend to raise the temperature, and thus the pressure. Endothermic processes clearly lower the temperature, but so also do energetically neutral ones, such as the production of H₂ as a product (as occurs in the AlN regions), because, as remarked earlier, energy must be supplied to bring the H₂ to the prevailing temperature.

* A more conventional isothermal phase-equilibrium diagram can also be constructed. Actual calculation has shown that the isothermal diagram at 3000 K differs only in detail from Figure 6 - notably in reduction of the zone where both AlN and Al₂O₃ are to be found.

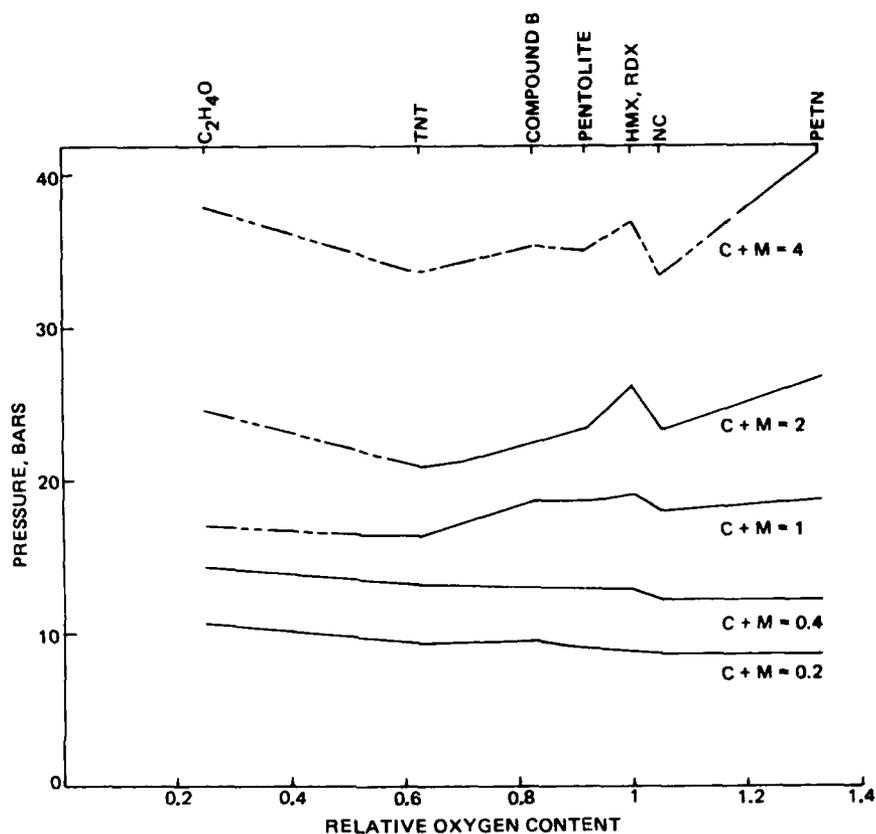
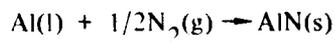


FIGURE 5. Total Pressure vs Relative Oxygen Content for Combustion of Eight Fuels in the Presence of Aluminum and Air.

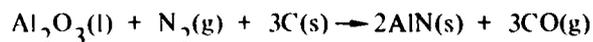
The effect on pressure is yet more complex, since it depends not only on temperature but also on the total number of moles of gas. Examined below are several important reactions which account for phase changes when $C + M$ is increased. It may be noted that for each case, because of conflicting effects, it is not possible to predict the pressure effect.

1. Simple production of aluminum nitride:



The reaction is strongly exothermic (though less so than the production of Al_2O_3) and thus increases the temperature. The number of moles of gas decreases.

2. Production of aluminum nitride at the expense of aluminum oxide:



This reaction is endothermic but increases the number of moles of gas.

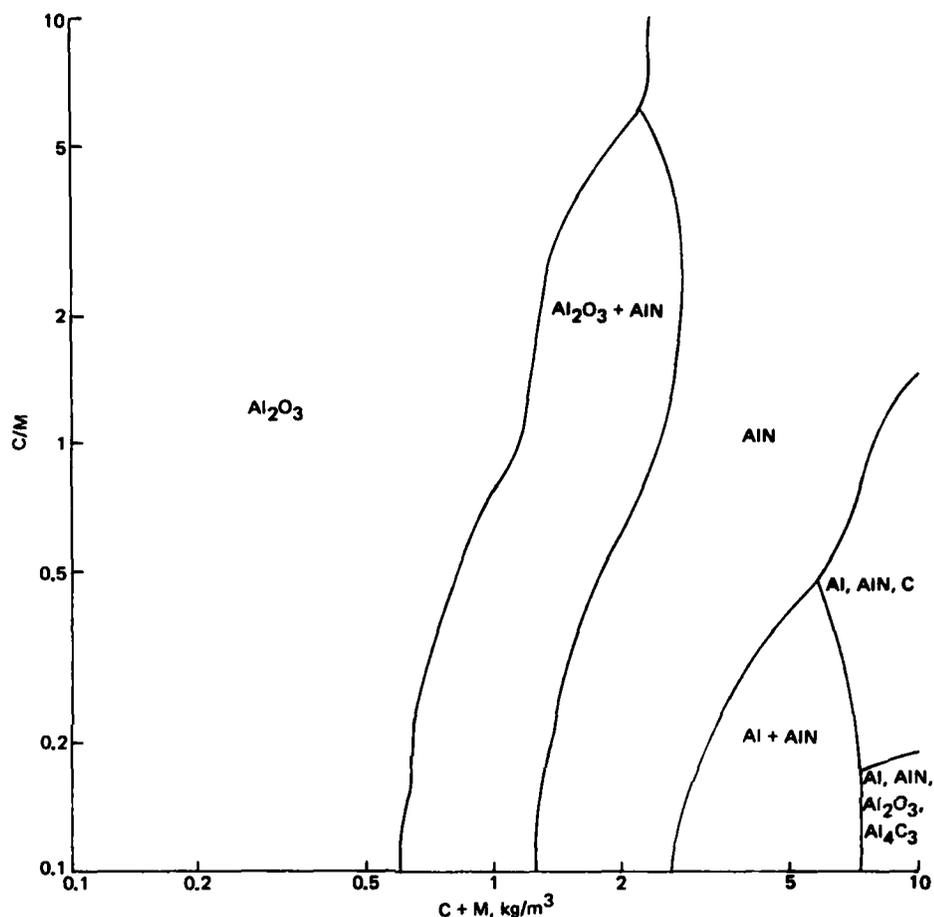
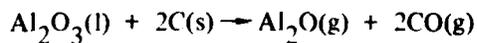


FIGURE 6. Condensed Phases in the Combustion Products of TNT and Aluminum in Air.

3. Disappearance of aluminum oxide, without concurrent formation of aluminum nitride:



Both reactions are endothermic but with a marked increase in the number of moles of gas.

A curious feature of Figure 6 is the "reappearance" of Al_2O_3 in the extreme lower right-hand corner. It is instructive to examine the point ($C/M = 0.1, C + M = 10 \text{ kg/m}^3$) for all the fuels run, as shown in Table 9. It appears that the presence or absence of $\text{Al}_2\text{O}_3(\text{l})$ is governed entirely by the equilibrium



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TABLE 9. Properties of Aluminum-Fuel-Air Mixtures
at C/M = 0.1, C + M = 10 kg/m³.

Fuel	T	Condensed phases	^a a _O - ^a a _C , moles
PETN	2656	Al(l), AlN(s), Al ₂ O ₃ (l)	37
NC	2569		31
Pentolite	2567		25
Comp B	2613		23
RDX	2745	Al(l), AlN(s)	29
HMX	2733		29
TNT	2529	Al(l), AlN(s), Al ₂ O ₃ (l), Al ₄ C ₃ (s)	13
C ₂ H ₄ O	2459		-4

^aSee text.

The formation-constant data are also used to compute the number of moles of Al₂O gas in equilibrium with the two liquids at several temperatures: 2500 K (13.4 moles); 2600 K (22.2 moles); 2700 K (35.0 moles). Thermodynamic principles require that the actual number of moles of Al₂O may not exceed the equilibrium value; if smaller than the equilibrium value, then equilibrium is not established and, for this case of large excess of aluminum, the Al₂O₃ must disappear.

The oxygen present in these systems is, for all but the last two cases, converted first to CO, then to Al₂O. First assuming no Al₂O₃ is formed, the mole number of Al₂O = a_O - a_C (moles of oxygen atoms less moles of carbon atoms in the mixture). If a_O - a_C < (Al₂O)_{eq} (the equilibrium value at the adiabatic temperature), then Al₂O₃ will not be observed. Such is the case with HMX and RDX at ca 2700 K. PETN is so oxygen-rich that even at 2700 K, Al₂O₃ would form; with nitrocellulose, pentolite, and Comp B, the adiabatic temperature is significantly lower, so that again a_O - a_C exceeds (Al₂O)_{eq}. The cases of RDX and HMX are thus another result of the considerably positive energy of formation.

The very oxygen-deficient TNT and C₂H₄O show another feature altogether. Here the temperature is so low and the carbon content so high that it is possible for Al₄C₃ to be produced. As a result there is made available considerable oxygen that would otherwise have been used in formation of CO, and once again Al₂O₃ can be produced. (In the isothermal diagram for TNT at 3000 K, cited in the footnote on page 21, Al₂O₃ is not seen.)

COMMENTS ON THE APPROXIMATIONS

The assumption that the process is adiabatic implies negligible energy losses due to radiation, conduction, and convection from the moment of initiation to the establishment of thermodynamic equilibrium. Of these, the losses due to radiation seem the more likely,

because of the very high temperatures involved. A recent study by LCDR D. E. Smith⁷ indicates, however, that where detonation has occurred the energy loss due to radiation will amount to less than 1/2% of the energy liberated isothermally. The model assumes black-body radiation, an assumption which is supported in the treatment, and considers the time for radiation to be no greater than 20 times the time required for arrival of the detonation front to the surface of the container.

Where deflagration is the sole combustion process, radiation effects may be expected to be considerable. Some consideration of this point has been made in the study of non-metallized fuels by Kinney, Sewell and Graham.¹

The ideal gas assumption is very good where the permanent gases are concerned: CO and H₂ are at temperatures one to two orders of magnitude greater than the critical temperatures, and maximum pressures are at most a few times the critical value. Since metallic aluminum is in the two-phase region, appreciable deviation from ideality must be considered; its critical temperature seems not to be known, but a rough guess of 5000 K would indicate a severe departure from ideality in these systems.

It is intended to address the question of corrections for nonideality at a future stage of the project. The effects of pressure on the apparent equilibrium constants as well as the effects on computation of the final pressure must be taken into account.

⁷ D. E. Smith, "Attenuation Effects of Thermal Radiation on Internal Blast Overpressure," M.S. Thesis, Naval Postgraduate School, December 1979.

Appendix A

STANDARD STATES, ACTIVITIES, AND FORMATION CONSTANTS

The activity of any chemical species in a system may be defined⁶ as

$$a_i = f_i/f_i^\circ \cong p_i/p_i^\circ \quad (\text{A-1})$$

where the f 's are the fugacities and the approximation to partial pressure assumes ideal-gas behavior; the superscript $^\circ$ refers to a *standard state* which may be chosen arbitrarily. Most commonly the standard state is that of unit fugacity for gases (whence activity is approximated by the partial pressure) and for the pure phase where condensed phases are concerned. In addition, *reference states* are commonly used in thermochemistry and thermodynamics, usually selecting the stable form of the element.

On this basis, we can write for any chemical species, $A_i = A_a C_b H_c N_d O_e$ the thermodynamic equilibrium constant of formation (from the elements in their reference states) as

$$K_f = a_{A_i} / (a_{Al}^a a_C^b a_{H_2}^{c/2} a_{N_2}^{d/2} a_{O_2}^{e/2}) \quad (\text{A-2})$$

bearing in mind that the reference states for hydrogen, nitrogen and oxygen are the diatomic gases.

In thermodynamic tables, such as the JANAF Tables, the reference state is commonly taken as the phase stable at the temperature of concern, and the standard state will change accordingly. Thus, for metallic aluminum the standard state is the pure liquid between the melting point (933 K) and the normal boiling point (2767 K) and is the state of unit fugacity above that temperature. This change in standard state leads to a discontinuity in the slope of the equilibrium constants and would require a different empirical equation to fit the data below 2767 K than above. It was thus felt to be far more convenient to select aluminum vapor at unit fugacity as the standard state throughout. This choice did, however, require recalculation of some of the JANAF formation-constant data before fitting. Since aluminum vapor was frequently an important component of the gaseous products, the choice was quite a reasonable one.

In the case of carbon, however, it scarcely seemed appropriate to select any of the gaseous elemental species (C , C_2 , or C_3) as the standard state, since this would require re-computing *all* of the data on carbon compounds; and, moreover, since the activity of carbon becomes very small at low temperatures in the presence of excess oxygen, it is entirely possible that the amount of gaseous carbon would be in error on account of computational underflow. (The HP 9845 cannot treat numbers less than 10^{-99} .) Graphite was therefore

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selected as the standard state. The activity now possesses a peculiar quality: if graphite is present, $a_C = 1$; if it is absent, however, it is not true that a_C is zero, nor is it undefined. Consider the following:

$$a_{\text{CO}_2} = K_{\text{CO}_2} a_C a_{\text{O}_2} \quad (\text{A-3})$$

When graphite is present, a_{CO_2} depends on a_{O_2} (or *vice versa*). But if graphite is not present and both a_{CO_2} and a_{O_2} are known (as is the case when a fuel is burned in a large excess of oxygen) the activity of carbon is given by

$$a_C = a_{\text{CO}_2} / (K_{\text{CO}_2} a_{\text{O}_2}) \quad (\text{A-4})$$

This concept has been used throughout, and it has proved a useful one.

Appendix B

THE NEWTON-RAPHSON METHOD FOR SIMULTANEOUS
NONLINEAR EQUATIONS

Suppose the variables to be x_j , $j = 1$ to n , given n nonlinear equations of the form

$$f_i(x_1, x_2, \dots) = 0, \quad i = 1 \text{ to } n \quad (\text{B-1})$$

Let x_j^0 be the initial approximation for each variable, from which can now be computed the set of $f_i^0(x_1^0, x_2^0, \dots)$. The objective is to improve the approximations so that each f_i becomes more nearly zero. If dx_j is the improvement to be made to x_j^0 , a new set of approximations is generated, $x_j^1 = x_j^0 + dx_j$ and a corresponding new set of f_i . Let the change in f_i be denoted df_i so that $f_i = f_i^0 + df_i$. Since f_i is a state function of the variables x_j , it follows from the principles of calculus that

$$df_i = \left(\frac{\partial f_i}{\partial x_1} \right) dx_1 + \left(\frac{\partial f_i}{\partial x_2} \right) dx_2 + \dots = \sum_{j=1}^n \left(\frac{\partial f_i}{\partial x_j} \right) dx_j \quad (\text{B-2})$$

Hence the improved set of equations will be

$$f_i^0 + \sum \left(\frac{\partial f_i}{\partial x_j} \right) dx_j = 0 \quad (\text{B-3})$$

If $[D_{ij}]$ is the matrix of $\frac{\partial f_i}{\partial x_j}$, $[\delta_j]$ the vector of dx_j , $[Y_i]$ the vector of f_i^0 , then the set of equations has the matrix form

$$\begin{aligned} [D_{ij}] [\delta_j] &= [Y_i] \\ \text{whence } [\delta_j] &= -[D_{ij}]^{-1} [Y_i] \end{aligned} \quad (\text{B-4})$$

The latest values of the variables are used to compute $[D_{ij}]$ and $[Y_i]$; a numerical evaluation of the partial derivatives is used. $[\delta_j]$ gives the next approximation from which a new set of $[D_{ij}]$ and $[Y_i]$ are found and the process is repeated to any desired precision.

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In this case each f_i represented the error in the material balance for an element. Iteration was continued until the error for each element was no more than one part in 10^4 , relative to the total amount of the element present.

Appendix C

ISENTROPIC PROCESSES FOR AN IDEAL GAS OF VARIABLE COMPOSITION

When the number of moles of gaseous components can vary, as a result of shifting chemical equilibria, the ideal gas law remains $P = nRT/V$, but now n is a variable, dependent on P and T . For an isentropic process⁴

$$dU = -PdV$$

or

$$C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = -PdV \quad (C-1)$$

$C_V = \left(\frac{\partial U}{\partial T} \right)_V$ and is evaluated by measuring internal energy (relative to any chosen zero datum) at two temperatures which are very close together and for which the same set of condensed phases will be present at equilibrium. The partial derivative in Equation C-1 is found from the thermodynamic equation of state⁴

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (C-2)$$

and, for variable n ,

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V} \left[n + T \left(\frac{\partial n}{\partial T} \right)_V \right] \quad (C-3)$$

When Equations C-2 and C-3 are substituted into Equation C-1,

$$C_V dT = - \frac{RT}{V} \left[n + T \left(\frac{\partial n}{\partial T} \right)_V \right] dV$$

that is,

$$\frac{C_V}{R} d \ln T = - \left[n + T \left(\frac{\partial n}{\partial T} \right)_V \right] d \ln V \quad (C-4)$$

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An "isentropic coefficient", λ , is now defined by the equation

$$\lambda = 1 + \frac{R}{C_V} \left[n + T \left(\frac{\partial n}{\partial T} \right)_V \right] \quad (C-5)$$

so that, by substitution into Equation C-4,

$$TV^{\lambda-1} = \text{constant}$$

C_V , as defined above, and λ , as defined by Equation C-5, have been computed for each point used in these calculations. Values for C_V vary widely, being especially large in regions where phase changes are taking place. A few values of C_V and λ are given in Table 8. (All these computed values have been retained on file for any interested person, as well as values of the average molar mass and the number of moles of gaseous products.)

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