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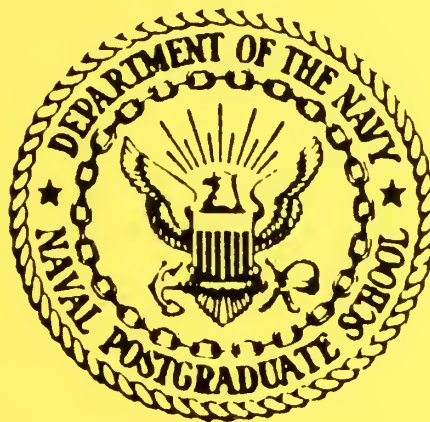
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NAVAL POSTGRADUATE SCHOOL Monterey, California



INTERNAL EXPLOSIONS OF REACTIVE ALUMINUM
WITH A PBX IN AIR

Richard A. Reinhardt

August, 1983

Approved for public release; distribution unlimited

Prepared for: Naval Surface Weapons Center
White Oak, Silver Springs, Maryland 20910

NAVAL POSTGRADUATE SCHOOL
Monterey, California

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INTRODUCTION

This report is concerned with an application of the computational methods developed previously (1,2) in this laboratory for the analysis of internal explosions of C-H-N-O fuels with aluminum in air. The present study was conducted in response to a direct request from the Naval Surface Weapons Center for an examination of internal explosions in air of reactive aluminum plus a PBX explosive.

The system investigated consisted of 208.5 lbs (94.6 kg) of reactive aluminum (95% aluminum, 5% nitrocellulose which is 12% nitrogen, by mass) and 52.1 lbs (23.6 kg) of a PBX material, represented by $C_{1.9} H_{3.471} N_{1.739} O_{1.827} Al_{0.747}$. Air volumes ranged from 2000 to 50000 cubic feet (56.6 to 1416 cubic meters).

As before (1), metal and fuel were considered to be introduced at 25°C into the air volume at one bar pressure. The combustion was treated as adiabatic and the products were assumed distributed uniformly in the total volume. All gases were treated as ideal and the volume of condensed phases was neglected. The air composition used was 78 mole % N_2 , 21 mole % O_2 and 1 mole % Ar.

BASIS OF CALCULATIONS

Details of the computational method are given in Ref. 1 and 2; a brief summary follows.

Internal energy must remain constant for an adiabatic, constant-volume process. Thus a temperature is found for which

the total internal energy of the equilibrium mixture of products is equal to the internal energy of the entering materials at 298 K.

The same 28 gaseous and 5 condensed-phase products were considered as in Ref. 1; the five parameters representing internal energy and the four for equilibrium constant of formation for each product were taken from that source. For the starting materials, the internal energy of formation of nitrocellulose (12%), which comprises 5% of the active aluminum, was taken to be -880.5 kJ per mole of $C_6 H_7 N_{2.25} O_{9.5}$ (3) and that of the PBX as -10.36 kJ per 100 g (4). (A few points were computed using -85 kJ per 100 g for the PBX (5); the results for the two sets were barely distinguishable, with difference in pressure of no more than 0.01 bar and in temperature of not more than 1 K.)

All calculations were performed on the HP 9845A desktop computer, using a program slightly modified from that described in Ref. 2.

RESULTS

Computations were carried out for fixed masses of metal and fuel in 23 different air volumes ranging from 2000 to 50000 cu ft. Table I shows the volume, overpressure (relative to one bar), product gas concentration in total moles of gas per cu m, and formulas of condensed phases. An asterisk is used to denote the air volume (11850 cu ft = 335.6 cu m) that corresponds to a mixture stoichiometric for the formation of Al_2O_3 , CO, H_2O and N_2 . Al_2O_3 , when present is found as the liquid above

the melting point, 2315 K (6), and as the solid below; both phases are observed at the next to the last point ($V = 45000$ cu ft = 1274 cu m). The overpressure and temperature results from Table 1 are shown graphically in Fig. 1 and 2, respectively.

Table 2 gives, for selected volumes, the total quantities of all products found in appreciable amounts; dashes indicate amounts less than 0.01 kmole (10 moles). Fig. 3 presents the product data in terms of partial pressures. All the volumes used for computation are included in the figure, but the curves are limited to products whose partial pressures reach at least 0.1 bar; nitrogen and argon, moreover, have been omitted for sake of clarity. The apparent inconsistencies between Table 2 and Fig. 3 (for example, the absence of H_2O from Fig. 3) are to be attributed to the relatively low temperatures and the dilution of combustion products by air at the higher volumes.

It will be noted that of the 28 gaseous species allowed for (1) only 17 appear in Table 1, and of the 5 possible condensed species only AlN and Al_2O_3 are found. It may be presumed that at gas volumes less than 2000 cu ft liquid Al and solid carbon would appear; it seems doubtful, however, judging from product yields found for other fuels (1), that there is sufficient carbon present in this system for the formation of solid aluminum carbide or the reduced carbonaceous gaseous species.

DISCUSSION

Fig. 2, showing T versus V, is equivalent to the plots of T versus C+M (mass of fuel plus metal, per unit volume) in Ref. 1,

with the recognition that a large air volume corresponds to a small value of C+M. The behavior of the plot is that of an oxygen-deficient fuel, with a temperature maximum close to the stoichiometric point. This behavior is expected, inasmuch as departing from the stoichiometric point in either direction results in an accumulation of energy-absorbing products: Al(g) and Al₂O on the low-volume side; O, NO and O₂ on the high-volume side. The temperature maximum is actually shifted to a slightly smaller volume than stoichiometric, reflecting the fact that hydrogen is only partly oxidized in this region: as can be seen from Table 2, rather less than half the hydrogen present has been converted to OH or H₂O at the stoichiometric point.

The pressure curve (Fig. 1) is complicated by two factors. In moving from the stoichiometric point to lower volumes, whereas the temperature decreases uniformly, the concentration of gaseous products (see Table 1) increases, at first slowly, and then quite rapidly at low volumes. There thus results a local minimum in pressure at about 5000 cu ft. It should also be remarked that this minimum in pressure is at about the point where AlN begins to form. As was noted before (1), the production of AlN at the expense of Al₂O₃ is a process that considerably increases the number of moles of gas.

APPROXIMATIONS

The assumption of adiabatic behavior appears warranted for detonations (7). The ideal gas approximation has been examined by Athow (8). Of the gaseous species found in the current system,

only Al vapor is below the critical temperature. (The other gases may be presumed to be so far above the critical temperature that for them the ideal-gas assumption may be taken for granted.) For Al the following critical constants have been estimated:

$T_c \sim 8000 \text{ K}$, $P_c \sim 4100 \text{ bars}$, $V_c \sim 0.05 \text{ dm}^3/\text{mole}$. The maximum partial pressure computed for Al (Fig. 3) is about one bar at a total concentration of 87.5 moles/m^3 , corresponding to a molar volume of $11.4 \text{ dm}^3/\text{mole}$. At the reduced pressure

$P_r = P/P_c \sim 10^{-4}$ and the reduced volume $= V/V_c \sim 200$ it

can be anticipated that no appreciable deviation from ideality should be found for Al vapor.

Table 1. Internal Explosions of 208.5 lbs Reactive Aluminum plus 52.1 PBX in Air.

Volume		Overpressure (bars)	Temperature (kelvins)	Concentration of Gaseous Products moles/m ³	Condense Phases
(cu ft)	(cu m)				
2000	57	15.63	3054	87.5	AlN
2500	71	14.27	3004	76.0	AlN, Al ₂ O ₃
3000	85	13.47	2993	68.8	"
4000	113	12.46	2976	59.7	"
5000	142	12.30	3106	54.4	Al ₂ O ₃
6000	170	13.09	3551	51.6	"
7000	198	13.22	3784	49.4	"
8000	227	13.10	3902	47.8	"
9000	255	12.90	3961	46.6	"
10000	283	12.67	3987	45.6	"
11000	311	12.46	3993	44.8	"
11850*	336	12.27	3986	44.3	"
13000	368	12.03	3961	43.6	"
14000	396	11.80	3925	43.2	"
15000	425	11.56	3875	42.8	"
17000	481	11.03	3740	42.2	"
20000	566	10.23	3508	41.6	"
25000	708	9.14	3176	40.9	"
30000	850	8.29	2905	40.6	"
35000	991	7.58	2672	40.4	"
40000	1133	6.97	2471	40.3	"
45000	1274	6.49	2315	40.3	"
50000	1416	6.27	2239	40.3	"

*Stoichiometric for Al₂O₃ + CO + H₂O

Table 2. Kilomoles of Products from the Internal Explosions of 208.5 lbs
 Reactive Aluminum plus 52.1 lbs PBX in Air.

Air Volume → cu ft)	2000	5000	10000	11850*	15000	25000	50000
	0.23	0.25	0.25	0.16	0.04	---	---
H	0.02	0.01	---	---	---	---	---
CO	---	0.03	0.18	0.17	0.09	---	---
CO ₂	---	---	0.03	0.04	0.04	---	---
H ₂ O	1.00	1.21	0.28	0.14	0.03	---	---
H ₂	0.02	0.06	0.11	0.14	0.17	0.28	0.55
NO	0.55	0.56	0.54	0.53	0.50	0.22	---
NO ₂	---	---	0.02	0.03	0.06	0.33	0.55
H ₂	0.06	0.10	0.50	0.49	0.40	0.07	---
H	---	---	0.10	0.14	0.23	0.29	0.05
CO ₂	0.43	0.41	0.12	0.10	0.08	0.02	---
H ₂ O	---	---	0.04	0.05	0.08	0.27	0.45
NO	---	---	0.16	0.27	0.53	1.03	0.69
CO	1.38	4.68	9.06	10.65	13.33	22.00	44.45
H ₂	---	---	0.24	0.42	0.49	0.48	0.03
NO ₂	---	---	0.03	0.08	0.19	2.19	8.51
UN(S)	1.25	0	0	0	0	0	0
NO (sor 1)	0	0.41	1.23	1.41	1.63	1.75	1.75

*Stoichiometric for Al₂O₃ + CO + H₂O

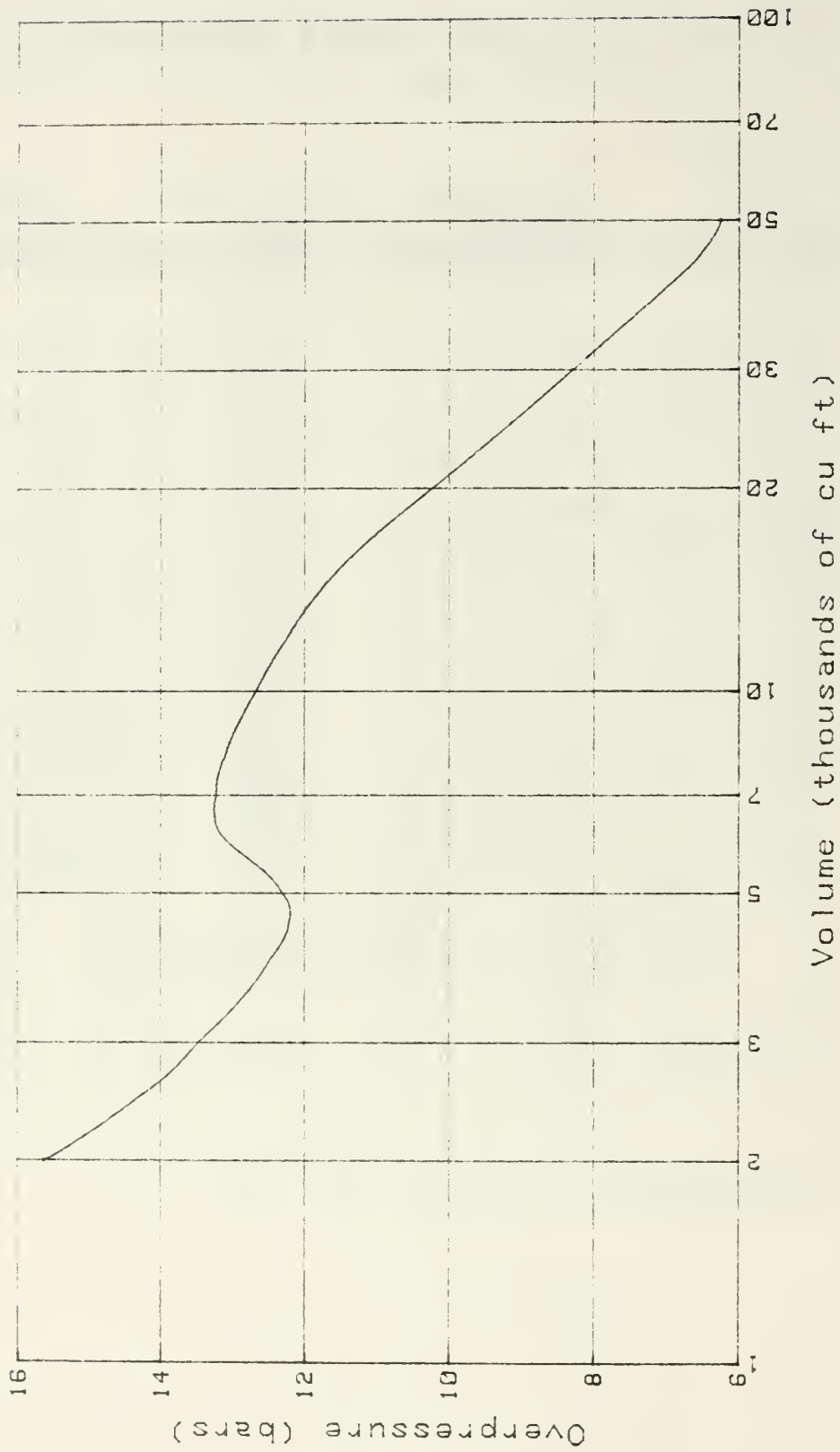


Figure 1. Overpressure versus air volume for internal explosions of 208.5 pounds reactive aluminum plus 52.1 pounds PBX.

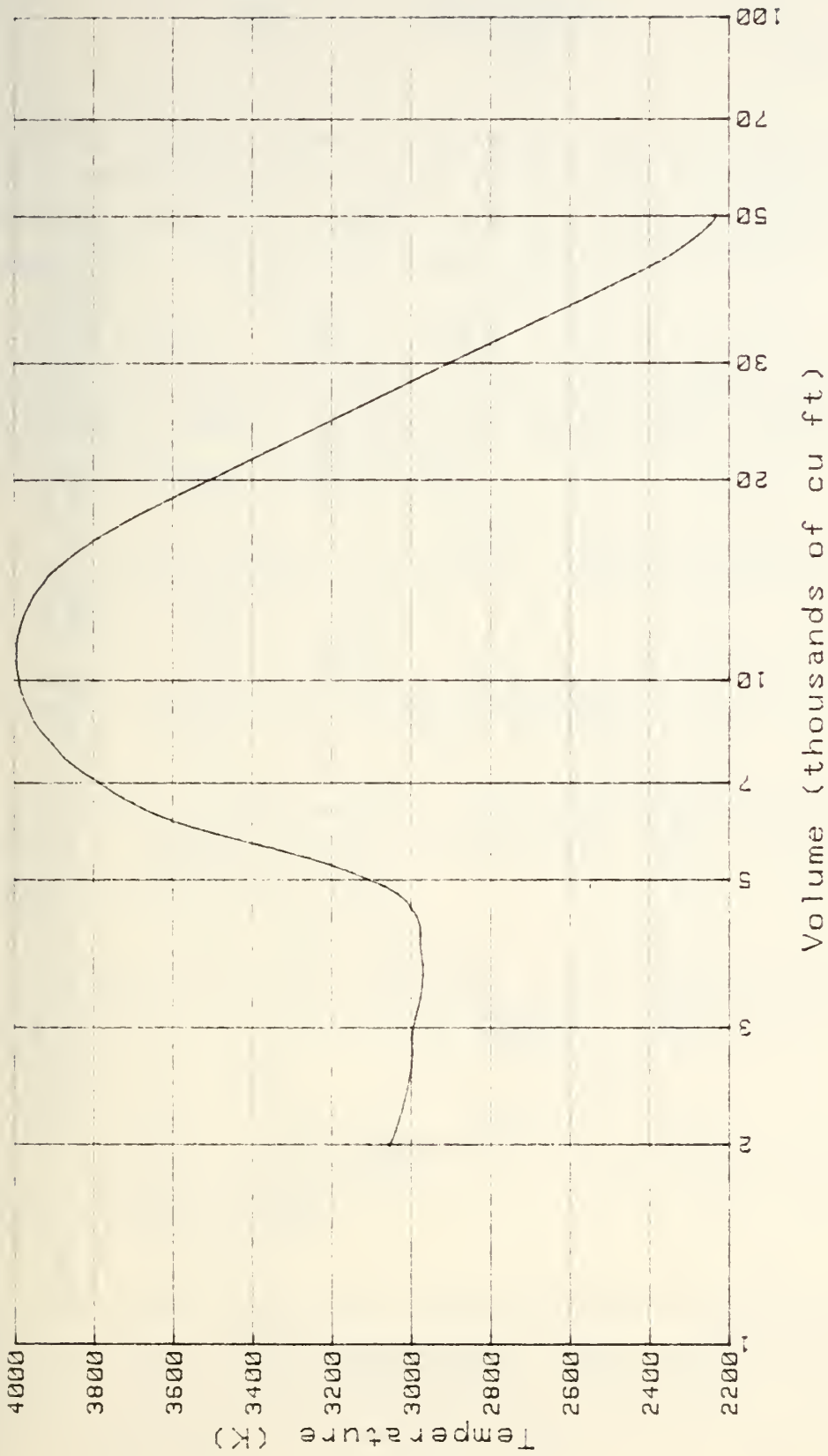


Figure 2. Temperature versus air volume for internal explosions of 208.5 pounds reactive aluminum plus 52.1 pounds PBX.

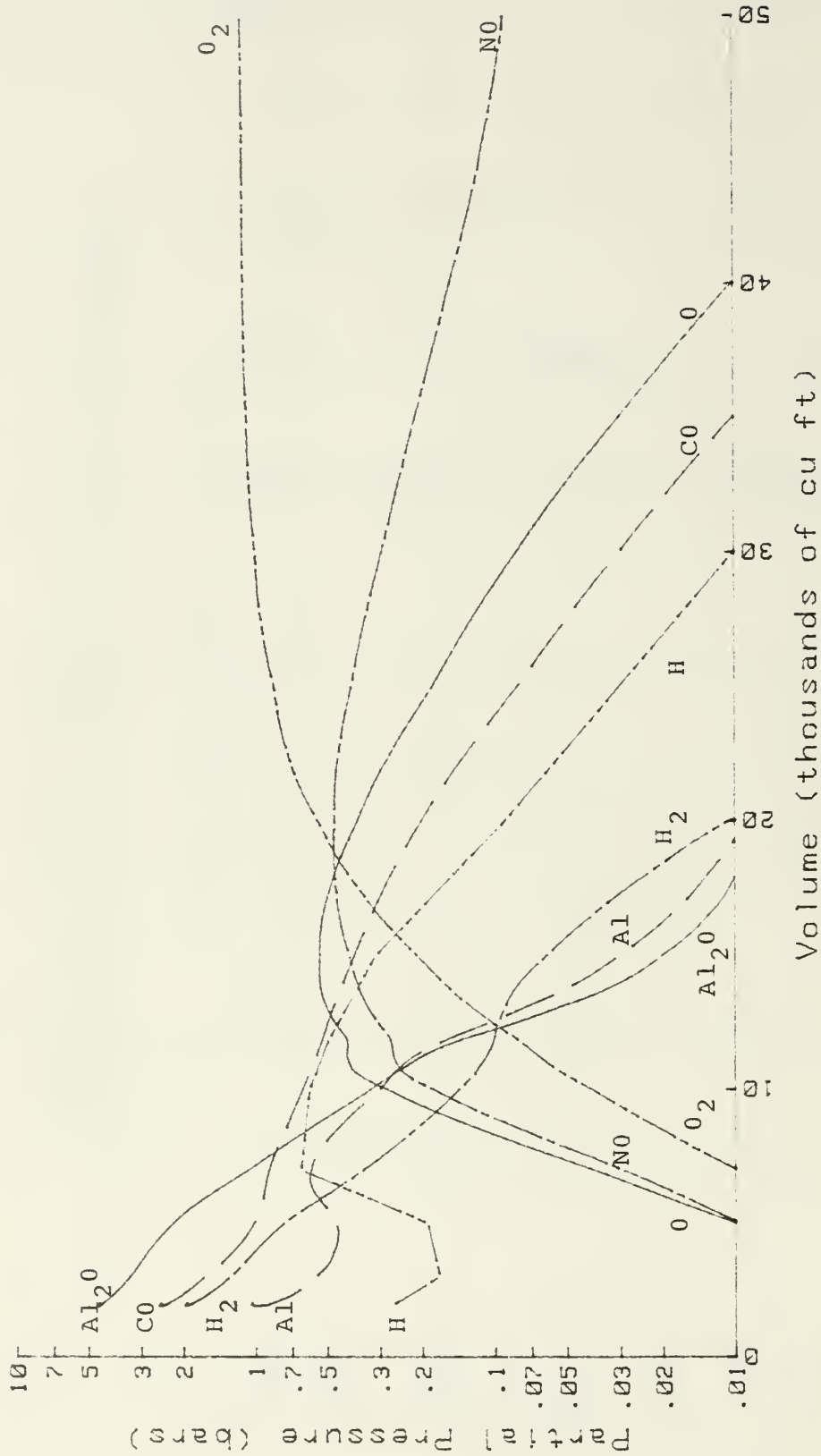


Figure 3. Partial pressures of product gases versus air volume for internal explosions of 208.5 pounds reactive aluminum plus 52.1 pounds PBX.

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