*Detonation Chemistry Apparatus Experiments
with Nonreactive Liquids, Reactive Liquids,
and a Reactive Solid*

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DETONATION CHEMISTRY APPARATUS EXPERIMENTS WITH NONREACTIVE LIQUIDS, REACTIVE LIQUIDS, AND A REACTIVE SOLID

by

John Lyman, Herb Fry, Dale Breshears, and Jerry Romero

ABSTRACT

The detonation chemistry apparatus was designed to analyze the results of detonating small quantities of explosives or the results of rapidly mixing reactants. The diagnostics are rapid Schlieren photography of the emitted plume (up to 10 photographs per microsecond) and rapid mass spectroscopy (12 μ s per scan). We report here the results of a series of experiments with two liquids that do not react exothermically and another series with liquids that do react exothermically. We also report some experiments with a solid reactant, Teflon.

Introduction

An earlier version of this report entitled "Mixing and Chemical Reactions in High-Velocity Experiments" was submitted to the 1995 Lethality Enhancement Annual Progress Report in November 1995. It, however, will be issued as part of a classified (SNSI) report. We felt that it would be useful to have an unclassified version of an extensive set of experiments with the Detonation Chemistry Apparatus (DCA).

Objectives of Experimental Program

During the last year the laboratory experimental program of the Reactive Munitions Project was designed to answer several questions about the reaction of an oxidizer with target material. These questions include the following:

- (1) How well do the launched and target materials mix on contact?
- (2) How fast do the mixed materials react?
- (3) What are the products of the chemical reaction?
- (4) What is the effect of an exothermic reaction on further mixing and reaction?
- (5) How do changes in the geometry of the experiment change the observations?
- (6) Are the assumptions for the chemistry and turbulence models appropriate in the reactive munitions code?
- (7) Can the processes occurring in a laboratory-scale experiment be simulated with the reactive munitions code?

The code used for these and larger tests includes 2-dimensional hydrodynamics, turbulent mixing, chemical reactions, and fracture. The data from the experiments provide a comparison with the calculations on a much smaller scale than the large, expensive projectile-impact tests. Although the experiments are on a smaller scale, they do have many features of the full-scale

experiments. They provide tests to which the calculations may be compared.

Detonation Chemistry Apparatus (DCA)

All laboratory-scale experiments for this last year were performed with the DCA. This apparatus was originally designed to examine in detail the processes that occur in an explosive reaction. As modified for the reactive munitions project, the DCA allows launching one material (liquid) into another with either a slapper detonator or an explosive initiated by the slapper. The materials burst the confining diaphragms and mix with each other in a manner determined by the geometry of the confining cells.

The DCA is equipped with Schlieren photography arrangement that takes a series of photographs of the expelled material. The time between photographs was 10 μ s for most of the experiments reported here. With the most recent modifications this time may be reduced to as low as 0.1 μ s.

The second diagnostic is a time-of-flight mass spectrometer that takes a mass spectrum out to mass 295 every 12 μ s. This diagnostic gives each mass as a function of time for about 4 ms (327 scans). The mass spectrometer may be initiated with the slapper discharge, or it may be delayed by a pre-set amount. The distance from the cell containing the liquids to the point of ionization of the gases is 1.29 m.

Figure 1 shows the layout of the DCA with the Schlieren optics and camera, the mass spectrometer, and the carousel containing the reaction cells. Normally two cells are loaded with liquids and connected to the slapper and the carousel. After the chamber has been evacuated, both are fired within a short time period. Both the mass spectrometer signals and the Schlieren photographs are stored electronically. The data files are then available to be further processed by computer methods.

During the year we have used two reaction cell configurations. An expanded view of the first, which we refer to as the "original cell design," is shown in Fig. 2. After the cell components are bolted together and loaded with the necessary liquids, the reaction cell consists of a support mount and five sections. Each of the sections is 3 mm diameter and 1/4 in. long. The slapper sits on the support

mount. An electrical discharge through the copper strip of the slapper accelerates the slapper material through the first section to the first diaphragm. Each of the next three sections (designated "1", "2", and "3") is either evacuated or contains a liquid material. The labeling of Fig. 2 shows "oxidizer" in Section 1, nothing in Section 2, and "fuel" in Section 3. The most commonly used fuel is triethyl phosphate (TEP). A shorthand notation for labeling the contents of the three sections is "/ox//TEP/" for the materials in Fig. 2. The final section is an extension that keeps the final diaphragm in place. The diaphragms are Kapton film unless the cell section contains oxidizer; then, it is nickel film.

A second cell design, designated as the "new cell design" or "nd", was constructed to enhance mixing of the liquids and to prevent the slapper material from reaching the mass spectrometer. Figure 3 shows that design. The main change in the new design is choking down Sections 1 and 3 to 1 mm diameter and reducing the diameter of Section 2 to 1 mm.

Some of the experiments described in a later section were with Teflon powder. In these cases the liquid-containing sections were removed and Teflon was packed into a pellet that was 3 mm diameter and about 1 mm high and placed in the position of Section 1 in Fig. 2.

Figure 1. Detonation Chemistry Apparatus with mass spectrometer and Schlieren optics.

Figure 2. DCA original cell design.

Figure 3. DCA new cell design.

Experimental Results--Nonreactive Liquids

Earlier experiments (Spring 1994) were somewhat difficult to interpret because they indicated that chemical reactants and reaction products were not arriving at the mass spectrometer in the expected order. To remove the effect of exothermic chemical reactions from the dynamics of the fluid flows, but to still consider the effect of mixing and reaction of the reactants, we replaced the two reactants with water (H_2O) and heavy water (D_2O). These species may still mix with each other, and even react (by hydrogen exchange to form HDO), but the reactions are thermoneutral and produce insignificant amounts of chemical energy. These experiments thus provide a test of the turbulence and mixing features of the code.

Both the original cell design and the new design were used in the water experiments. In Table 1 we have characterized the experiments by giving the time required for the first material to exit the cell (t_{exit}), the speed towards the detector (v_z), and the radial expansion speed (v_r). These were all inferred from the Schlieren photographs. Additionally, Table 1 includes three speeds (v_1 , v_2 , v_3) obtained from the mass spectrometer. These were obtained from what appear to be three different types of material. Often, the first material to arrive was a very small amount of what appeared to be gas trapped in one of the cells (v_1 , Material 1). This material often contains nitrogen. The second material (v_2 , Material 2) was a small fraction of the total that gave a temporally smooth signal. This we interpret to be gases. The bulk of the material came later in a series of large spikes (v_3 , Material 3). This material correlated best with the photographically determined speed and was probably liquid. We can see the correlation of the photographically determined speeds with those obtained from the mass spectrometer by making plots of the speeds v_1 , v_2 , v_3 against the v_z . Figure 4 shows the correlation of the speed of Material 3 with the photographic speed. The slope of the fit to the points is near one as would be expected if the materials are the same in the two measurements. The other two speeds, v_2 and v_3 , are generally higher than v_z , and the correlation with v_z is poor. The average speed of Material 1 is 2372 ± 580 m/s. The average speed of Material 2 is 872 ± 338 m/s.

Table 1

Speeds Inferred from DCA Experiments with Water Species

Exp. No.	Cells ^a	t _{exit} ^b	v _z ^c	v _r ^d	v ₁ ^e	v ₂	v ₃	Comments
110194C	D__od	3	1706	61	2240	3583	1250	
110194D	D__od	5	1834	142	2107	3071	1280	
110294B	DD_od	10	704	64	2896	648	597	
110294C	DD_od	9	623	107	2028	671	371	
110994B	HD_od	10	1237	49	2829	1181	1327	
110994C	HD_od	21	508	91	1843	759	486	
111594B	HD_od	25	395	48	3162	1733	655	MS, 1.5 ms delay
111594C	HD_od	13	1254	40	- -	560	325	1 frame delay-misdirected.
113094B	H_Dod	57	294	59	- -	- -	- -	No mass spectrum
113094C	H_Dod	30	708	143	2443	860	645	
111894B	DH_od	8	955	47	5119	1612	526	One cell empty.
111894C	DH_od	10	661	50	2028	814	484	
121694B	D_Hod	36	609	134	1229	806	586	
121694C	D_Hod	38	470	111	1955	1194	512	
010695B	D_Hod	39	480	68	- -	411	210	MS delayed 3 ms.
010695C	D_Hod	22	384	65	- -	- -	300	MS delayed 3 ms.
020695B	D_Hod	--	480	--	- -	- -	248	MS delayed 3 ms.
020695C	D_Hod	20	384	119	- -	- -	335	MS delayed 3 ms.
083195B	D_Hnd	15	1089	49	2986	1236	1025	
083195C	D_Hnd	- -	- -	- -	2756	603	362	No Schlieren photo.
090195B	D_Hnd	18	789	33	2240	903	- -	
090195C	D_Hnd	28	664	36	2829	741	569	

^aChamber filling arrangement. In sections one, two, and three, D = D₂O, H = H₂O, _ = vacant section. "od" indicates original cell design, and "nd" indicates new cell design.

^bTime (μs) that fluid exits cell. Obtained from extrapolation of Schlieren photographs.

^cSpeed(m/s) that tip of plume moves away from cell. Obtained from Schlieren photographs.

^dRadial expansion speed(m/s) of plume. Obtained from Schlieren photographs.

^eSpeed(m/s) ejected material moves toward detector. Obtained from time dependence of mass spectrum. The subscripts refer to the three materials in the mass spectrum. "1" is air trapped in the cell, "2" is gas generated by the liquids, "3" is the bulk of liquid material.

^fMS = mass spectrometer. ₃

Figure 4. Speed v_3 vs. speed v_z . Points are experimental measurements and the line is a fit to the points. Includes all data from Table 1 with two chambers filled except for experiments with obvious problems, such as an apparent near empty chamber.

Figure 5a and 5b show the results of the simplest experiment. Only the first of the three sections had liquid D_2O . The others were empty (first entry of Table 1). We can see (Fig. 5a) the liquid D_2O appearing on the second frame ($10\ \mu s$). On the fourth frame a blooming of the plume already occurs. This blooming at the base of the plume was observed in several photographs and was not included in the entry for radial speed in Table 1. Figure 5b shows the temporal scan from the mass spectrometer for two masses. Mass 28 is N_2 , and the peak beginning at about scan 48 is Material 1 (Table 1). The first peak in the mass 20 (D_2O) is Material 2, and the spiky part of that trace, beginning about scan 82, is Material 3.

25000.0 50000.0

_10194C_IMG

Figure 5a. Schlieren photograph for experiment 110194c, D_2O in Section 1, original design. First photograph is lower right (time zero); second, lower left ($10 \mu s$); third, second up on right ($20 \mu s$), and so on.

Figure 5b. Time dependence of masses 20 and 28 from experiment 110194c /D₂O/.

Calculations of the processes for this experiment with the Reactive Munitions code showed that the bulk of the expelled plume was near liquid density (Material 3) but that it was preceded by a lower density gas (Material 2). The calculations also showed that the copper plasma from the slapper mixed with vapor from slapper-heated water, which bypassed the bulk of the expelled water and contributed to Material 2. The blooming beginning at Frame 4, Fig. 5a, is probably this hot material heated by the copper plasma. The calculations reproduce both the shape of the exiting plume and the later blooming.

An example of an experiment with two liquid materials separated only by a diaphragm is in Figs. 6a and 6b. The liquid plume appears more slowly than for loading a single section (Fig. 5a), and the radial expansion is slow until the last three frames where we see the blooming that dominated the photographs with only a single section filled. In the mass spectral scans (Fig. 6b) we see all three

materials. Material 1 is at the extreme left (mostly cut off), Material 2 is the smooth peak near 1.8 ms, and Material 3 begins at 2.7 ms. Mass 20 is entirely D_2O , mass 18 is mostly H_2O with some HDO and D_2O , and mass 19 is entirely HDO. (For intense signals mass discrimination is not perfect and some spillover occurs to adjacent masses). We see that mixing is nearly complete for Material 2 and that significant reaction has occurred to form HDO. At later times the D_2O , which should be the first material to leave the cell, is the largest signal, but the other two species are in large abundance. The extent of mixing is high, but incomplete. The extent of reaction to HDO is also large, but again, not complete.

Figure 6a. Schlieren photograph for experiment 110994c, H_2O in Section 1, D_2O in Section 2, original design. Frame numbering is the same as Fig. 5a.

Figure 6b. Time dependence of masses 18, 19, and 20 for experiment 110994c, H_2O in Section 1, D_2O in Section 2, original design.

With a gap added between two liquids we see some changes in both the Schlieren photos and the mass spectral signal (Figs. 7a and 7b). The additional diaphragm further slows the liquid plume (Fig. 7a), but the radial expansion appears to be more rapid. In the mass spectral scans (Fig. 7b) we again see that mixing and reaction is nearly complete in the region of Material 2 (1.8 ms) and extensive at later times. Note that the two water species seem to be inverted. The material closest to the detector arrives later.

Figure 7a. Schlieren photograph for experiment 121694b, D_2O in Section 1, H_2O in Section 3, Section 2 empty, original design. Frame numbering begins at upper right, to lower right, then to upper second from right, and so on.

Figure 7b. Time dependence of masses 18, 19, and 20 for experiment 121694b, D₂O in Section 1, H₂O in Section 3, Section 2 empty, original design.

The new cell design changes both the Schlieren photographs and the mass spectra. Figures 8a and 8b (last entry, Table 1) are an example of these experiments. One of the reasons for making the constrictions in this design (Fig. 3) was to prevent the blooming from the copper plasma that occurred late in the original design. We see from Fig. 8a that no blooming occurs over the range of the photographs and that a narrower aperture produces a much narrower plume. The Reactive Munitions code predicted both the lack of blooming and the narrow plume. The only species seen (Fig. 8b) over the 4 ms of the mass spectral operation were a small amount of nitrogen (mass 28) and H₂O (mass 18). The mass spectral trace for mass 19 showed nothing (similar to the mass 20 trace). The code predicted that we would have seen some of mass 20 before 4 ms. Currently, the code does not have the diaphragms in the calculation. This may contribute to this disagreement.

Figure 8a. Schlieren photograph for experiment 090195c, D_2O in Section 1, H_2O in Section 3, Section 2 empty, new design. Frame numbering is the same as Fig. 7b.

Figure 8b. Time dependence of masses 18, 20, and 28 for experiment 090195c, D_2O in Section 1, H_2O in Section 3, Section 2 empty, new design.

We can make some general observations after consideration of all of the Schlieren photographic and mass spectroscopic data from these water experiments. The Schlieren photographs indicated that for both designs the material was forced from the cells in a jet with very little radial expansion. The speed determined from the photographs and the mass spectrometer depended on the filling arrangements. Table 2 lists the average speeds for each of the entries in Table 1 for different cell filling configurations. The

speed of the bulk of the material (Material 3) measured with the mass spectrometer agreed best with the photographic measurements. With the original design considerable mixing (both H_2O and D_2O present) and reaction (to HDO) occurred in Material 3. In most cases the mixing and reaction was even more complete for Material 2. We concluded from model calculations and isotope analysis that these early materials were from hot species near the slapper that moved rapidly and entrained other materials. In experiments with the new design, mixing and reaction are greatly reduced, at least in the first 4 ms.

Table 2
Average Speeds for Different Cell Configurations

Cell Filling	t_{exit}^a	v_z^b	v_r^c	v_1^d	v_2	v_3
1 section	4.2	1770	102	2174	3327	1265
2 sections, no gap	14.1	688	68	2464	968	653
3 sections, with gap	34.6	476	100	1876	818	405
3 sections, new design	20.2	847	39	2703	871	652

^aTime (μs) that fluid exits cell. Obtained from extrapolation of Schlieren photographs.

^bSpeed(m/s) that tip of plume moves away from cell. Obtained from Schlieren photographs.

^cRadial expansion speed(m/s) of plume. Obtained from Schlieren photographs.

^dSpeed(m/s) ejected material moves toward detector. Obtained from time dependence of mass spectrum. The subscripts refer to the three materials in the mass spectrum. "1" is air trapped in the cell, "2" is gas generated by the liquids, "3" is the bulk of liquid material.

Experimental Results--Reactive Liquids

We have performed experiments with both cell designs with reactive liquids, triethyl phosphate (TEP) and oxidizer. These experiments differed in several respects from the water experiments. The photographs indicate higher velocities as well as rapid radial expansion of the plume. We observed reaction products at very early times for the original cell design and some at later times with the new design. We never saw the mass spectrum of the material in Section 1.

Table 3 summarizes speeds and observations of experiments with oxidizer and TEP with both cell designs. The items in Table 3 are similar to those of the water experiments in Table 1. The first column is the experiment number and the second is the filling arrangement and the cell design used. For all experiments the second section was vacant and either TEP or the oxidizer was in the first section and the other was in the third section. The columns labeled t_{exit} , v_z , and v_r were all obtained from the Schlieren photographs and have the same meaning as the same entries in Table 1. The time to exit the cell (t_{exit}) was similar to the experiments with water (Table 1). For the original design, $t_{\text{exit}} = 42 \pm 2 \mu\text{s}$, compared to $35 \pm 16 \mu\text{s}$ for the water experiments. For the new design, $t_{\text{exit}} = 25 \pm 3 \mu\text{s}$ compared to $20 \pm 7 \mu\text{s}$ for the water experiments. The speed towards the detector with the original design was greater for the reactive experiments, $v_z = 1323 \pm 116 \text{ m/s}$, than the water experiments, $v_z = 476 \pm 205 \text{ m/s}$. For the new design the speeds were similar, $853 \pm 155 \text{ m/s}$ for reactive experiments, and $847 \pm 218 \text{ m/s}$ for water experiments. The radial speeds were much greater for the reactive experiments for both designs. For the original design, $v_r = 994 \pm 180 \text{ m/s}$ for reactive experiments and $v_r = 100 \pm 38 \text{ m/s}$ for water experiments. For the new design, $v_r = 678 \pm 56 \text{ m/s}$ for reactive experiments and $v_r = 39 \pm 9 \text{ m/s}$ for water experiments.

Table 3

Speeds Inferred from DCA Experiments with Reactive Liquids

<u>Exp. No.</u>	<u>Cells^a</u>	<u>t_{exit}</u>	<u>v_z</u>	<u>v_r</u>	<u>v_{ox}^b</u>	<u>v_{TEP}^c</u>	<u>v_{prod}^d</u>	<u>v₃^e</u>	<u>Comments</u>
031595B	O_Tod	44	1150	725	- -	- -	--		No MS
032795B	T_Ood	43	1334	1197	2910	- -	2910	1310	
032795C	T_Ood	38	1486	1061	2830	- -	2760	- -	
041895B	O_Ood	20	500	525	- -	- -	- -	509 ^f	Oxidizer only
041895C	O_Ood	15	561	474	- -	- -	- -	587 ^g	Oxidizer only
042795B	O_Tnd	35	1010	612	- -	2829	- -	1010	Photo indicates leak
042795C	O_Tnd	- -	- -	- -	- -	1270	4890	1270	
050495B	O_Tnd	21	815	640	- -	1560	- -	761	
050495C	O_Tnd	30	887	816	- -	1820	- -	881	
051295B	T_Ond	26	609	707	1170	- -	- -	672	
051295C	T_Ond	25	709	640	1850	- -	- -	717	
092195B	O_Tnd	28	1285	626		2500	- -	1168	

^aChamber filling arrangement. In sections one and three, O = oxidizer, T = TEP. Section two is vacant for all experiments. "od" indicates original cell design, and "nd" indicates new cell design.

^bSpeed of oxidizer (m/s)

^cSpeed of TEP (m/s)

^dSpeed of reaction products (m/s)

^eSpeed of Material Three, see Table 1.

^fThe temporal behavior of this experiment was the same as the water experiments. This speed is the speed of Material Three described in the discussion of Table 1. The speeds of the other two materials are 2829 m/s for Material One and 1054 m/s for Material Two.

^gSee "f". The speeds of the other two materials are 1991 m/s for Material One and 1194 m/s for Material Two.

As in the case of the water experiments, in the reactive experiments the mass spectrometer temporal traces show several different types of materials. We observed no clear distinction between what we referred to as Material 1 (trapped air and other gases) and Material 2 (gases from the loaded liquids) in the reactive experiments. It is difficult to distinguish between the TEP mass spectrum or reaction products and trapped air. Most experiments, however, did show a smoother temporal trace at early times, which for the original cell design, contains reaction products. This is normally followed by a more spiky temporal trace, which we still refer to as Material 3, the higher density liquid component. The correlation between the speed of this material and the photographic speed, v_z , is even stronger than for the water experiments. Figure 9 shows a graph of the speed of Material 3, v_3 , versus the photographic speed, v_z . The slope near one, the intercept near zero, and the near straight line show that the material in the Schlieren photographs and Material 3 is the same. If the intercept were forced to be 0.0, the slope would be almost exactly 1.0.

Figure 9. Speed v_3 vs. speed v_z for all reactive experiments in Table 3 except for those where some obvious problem occurred. Points are experimental measurements and the line is a fit to the points.

We also note a fourth region of the temporal traces that was not present in the water experiments, that is, a region following the intense spikes of Material 3 where the signal intensity is very low, but still barely present. A careful examination of the mass spectrum of this region for one experiment showed that some reaction products were present. We conclude that this low signal intensity region is the material remaining after the rapid radial expansion, which was in turn caused by rapid chemical reaction.

In the next few figures we show both Schlieren photographs and mass spectrometer data for several experiments with reactive munitions. The speeds were all summarized in Table 3. The first of these are for the original cell design with TEP in the first section and oxidizer in the last section, Experiments 032795b and 032795c. Figure 10a shows the development of the rapidly expanding gas plume. Note that the radial expansion of the hot material is nearly as fast as the movement towards the detector. We can contrast this figure with that of an experiment with nonreactive water species, but with similar cell arrangement, Fig. 7a. The biggest difference we see is the rapid radial expansion in the reactive experiment.

Figure 10a. Schlieren photograph for experiment 032795b, TEP in Section 1, oxidizer in Section 3, Section 2 empty, original design. Frame numbering begins at upper right, to lower right, then to upper second from right, and so on. The photographs begin at 20 μ s after slapper.

Figure 10b shows three traces from the mass spectrometer for this experiment. The TEP and oxidizer traces are of single fairly strong lines of the mass spectra of the two species. The trace labeled "products" is the average of several masses that we interpret to be from six products of the reaction between TEP and the oxidizer. The figure caption lists those products. The mass spectrum also contains HF and HCl, but these were not included in the average because of the spillover from masses of F and Cl. (In a later figure we show the mass spectrum where the product peaks

are particularly strong). A somewhat quantitative assessment of the reactions products from the heights of the peaks contributing to the different product species gives the following percentages of species: CF_4 (with perhaps some PF_3 or PF_5), 60%; CO , 15%; PF_5 (with PF_3), 13%; HF , 12%; and smaller or undetermined amounts of HCl , COF_2 , and POF_3 . The important observations from Fig. 10b are that the products appear very early, that they are accompanied by the oxidizer, and that TEP, the material in the first section, does not appear anywhere in the first 3 ms. The Schlieren photograph does not see the material where the products appear, but only the material in the peaks around 1.25 ms.

Figure 10b. Time dependence of the mass spectral signals for Experiment 032795b for oxidizer, TEP, and the average of major peaks contributing to CO , CF_4 , COF_2 , PF_3 , PF_5 , POF_3 .

Figures 11a and 11b are the results of a similar experiment to those of the previous experiment. Note that the Schlieren photographs (Figs. 10a and 11a) are nearly identical. The mass spectra (Figs. 10b and 11b) are also similar. The oxidizer and reaction products appear early, but the large oxidizer signal does not appear in Fig. 11b. The times of appearance of the oxidizer and products are nearly identical in these two experiments (see also Table 3).

Figure 11a. Schlieren photograph for experiment 032795c. The photographs begin at 20 μ s after slapper. Cell filling, frame numbering, and time delay are the same as Fig. 10a.

Figure 11b. Time dependence of the mass spectral signals for Experiment 032795c for oxidizer, TEP, and the average of major peaks contributing to CO , CF_4 , COF_2 , PF_3 , PF_5 , POF_3 .

If we look carefully at Fig. 11b, we see that at about 0.6 ms reaction products dominate the mass spectrum. Figure 12 shows the mass spectrum for this experiment at that time. The main unlabeled peaks are due to a small amount of the oxidizer and its decomposition products at masses 73 and 54. The oxidizer decomposition products and ion fragmentation also contribute some to peaks labeled HF and HCl.

Figure 12. Mass spectrum of Experiment 0327905c at 0.6 ms. The labels account for most of the peaks.

Experiments with reactive liquids in the new cell design show some differences in both the Schlieren photographs and the mass spectrum. Figure 13a shows the Schlieren photographs for one such experiment for the oxidizer in the first section and TEP in the third. Note that the shape of the plume differs somewhat from that of the original design (Figs. 10a and 11a). Radial expansion still occurs, but some of the first material to exit does not expand so rapidly. This is apparently some of the unmixed, cooler TEP initially in 1 mm part of the third section (see Fig. 3). The mass spectrometer also indicates that the initial material is TEP (Fig. 13b). In fact, the only material seen in the mass spectrum is TEP or TEP decomposition products.

Figure 13a. Schlieren photograph for experiment 050495c. Oxidizer in Section 1, TEP in Section 3, Section 2 empty, new design. The photographs begin at 20 μ s after the slapper. Frame numbering is the same as Fig. 10a.

Figure 13b is temporal dependence of three ions from the mass spectrum of Experiment 050495c. The curves were temporally smoothed to remove some of the noise and all were scaled before smoothing to give the same maximum peak height. All three ions are part of the mass spectrum of TEP. $(\text{PO}(\text{OC}_2\text{H}_5)_3)^+$ is the parent ion, and the other two are ion fragments). The lightest ion, C_2H_5^+ , could also be from a decomposition product. We see that the relative intensity of that ion signal increases above the other two as time progresses. This indicates that the later TEP is more decomposed, apparently due to the chemical reaction occurring with the oxidizer.

Figure 13b. Time dependence of three mass spectral signals for Experiment 050495c. See Fig. 13a. The masses of the three ions are respectively, 29, 154, and 182.

In Fig. 14a we see a similar experiment to the previous one, but with the TEP and oxidizer reversed. We see again that the shape of the plume differs from that on the original design (Figs. 10a and 11a). Radial expansion of the tip of the plume is less than the original design, but more than when the liquids were reversed (Fig. 13a).

Figure 14a. Schlieren photograph for experiment 051295b. TEP in Section 1, oxidizer in Section 3, Section 2 empty, new design. The photographs begin at 10 μ s after the slapper. Frame numbering is the same as Fig. 10a.

The major signals in the mass spectrum were due entirely to the oxidizer and oxidizer decomposition products (Fig. 14b). However, as in the case of when the reactants were reversed, this reactant becomes more decomposed with time. This again indicates the effect of reaction at high temperature deeper into the cell. We see in Fig. 14b that the larger ion fragments dominate at earlier times and the smaller ones (like F^+) at later times.

Figure 14b. Time dependence of four mass spectral signals for Experiment 051295b, new cell design. See Fig. 14a. The masses of the ions are, respectively, 92, 73, 54, and 19.

We saw no reaction products in Experiment 051295b. In fact, the only experiment with the new cell design that showed significant reaction products was one where from the diagnostic evidence, one of the cell sections had leaked (Experiment 042795c, Fig. 3). We suspected that some evidence of reaction products may be buried in the signal noise. We returned to the original mass spectral data prior to binning into integer mass bins for Experiment 051295b and averaged the signals over time from 3.18 ms to 3.85 ms. This would be from about the end of the data traces in Fig. 14b to the end of the time of the experiment. (Figure 14b does not include all of the data of the experiment, but no prominent features occurred after 3.18 ms). After looking at the mass spectrum after this averaging, it was clear that some reaction products were present. We were able to assign 94% of the signal above background in this temporal region. The result of this assignment is in Fig. 15.

Figure 15. Results of analysis of Experiment 051295b by time average of the region between 318 ms and 3.85 ms. All but 6% of the ion signal was assigned.

One of the experiments with the new design resulted in damage to the cell. The code predicted damage for this design. More comparisons need to be made between the code experiments and the experimental results.

Conclusions--Liquid Experiments

The first section (Objectives of Experimental Program) listed several questions that we attempted to answer with these experiments. Some were answered by the experiments:

- (1) The experiments with water and the original design showed that mixing was extensive, but not complete. In experiments where

both isotopic forms of water are present, we see nearly complete mixing in the early vapor materials and less complete mixing in the later arriving bulk of the liquids (see Figs. 6b and 7b). On the other hand, the constrictions in the new cell design completely stopped mixing of the two water species, at least in the first four milliseconds of the mass spectrometric observations (see Fig. 8b). With reactive liquids we see evidence of reaction with both cell designs, which requires mixing, but we have not seen any mixing that did not lead to reaction. Reaction appears to separate the unreacted reactants (see Figs. 10b, 11b, 13b, and 14b).

(2) Reaction occurs rapidly within the cells. Even in the water experiments mixed species tend to react to form HDO when they mix (see Figs. 6b and 7b). The enhanced speeds with reactive species, both towards the detector and radially (Tables 1 and 3), indicate rapid reaction. The observation of reaction products (Fig. 12) supports the conclusion of rapid reaction.

(3) With the original design the observed reaction products tend to be those that result from complete devouring of the TEP molecules by the oxidizer. These are species that require many reaction steps like CF_4 and POF_3 (Fig. 12). The only observation of reaction products with the new cell design (Fig. 15) was of species that required only a few reaction steps like HF and HCl. This implies either a shorter time for reaction or different reaction conditions. Both reactants tend to decompose (Figs. 13b and 14b) due to unobserved exothermic reaction between TEP and oxidizer.

(4) As noted in (1), the exothermic reaction tends to separate the reactants and inhibits additional mixing.

(5) We have noted several differences between the two cell designs, the most important of which is the restricted mixing in the new cell design.

(6) Additional comparison of the predictions of the reactive munitions code with these experiments will indicate the appropriateness of the chemistry and turbulence models.

(7) The reactive munitions code has already been successful in simulating some of the experiments discussed here. Additional work will be necessary.

Experimental Results--Teflon

In keeping with our plans to do more experiments with solid reactants we have examined some earlier DCA experiments with Teflon. In these experiments the liquid-containing cell was replaced by Teflon powder compressed to different densities. The diagnostics were the same as the experiments discussed earlier, the mass spectrometer and Schlieren photography. The time between mass spectral traces was still 12 μ s and the time between photographs was 10 μ s unless otherwise noted.

We hoped to provide evidence of an energetic reaction and to identify the reaction products. The experiments were successful on both counts. Table 4 summarizes the experiments and gives pertinent speeds resulting from slapper launching. We have no results where we obtained good data from both the mass spectrometer and the Schlieren photographs on the same experiment. Some of this was by design. We blocked the mass spectrometer on the first experiment to protect the skimmer from damage. Notice that the speeds are high for all experiments and that the speed was highest for the least dense Teflon. Also, the radial expansion was rapid, indicating a very exothermic reaction.

Table 4
Speeds Inferred from DCA Experiments with Teflon

<u>Exp. No.</u>	<u>ID</u> ^a	<u>t</u> _{exit} ^b	<u>v</u> _z ^c	<u>v</u> _r ^d	<u>v</u> _{tef} ^e	<u>Comments</u>
081294e	56	2.9	2689	2493	- -	No MS
090794b	40				3590	No photo
090894b	55	7.5	2689	1037		No MS

^a Teflon relative theoretical density (%).

^b Time (μ s) that fluid exits cell. Obtained from extrapolation of Schlieren photographs.

^c Speed(m/s) that tip of plume moves away from cell. Obtained from Schlieren photographs.

^d Radial expansion speed(m/s) of plume. Obtained from Schlieren photographs.

^e Teflon speed from mass spectrum (m/s).

Figure 16 shows the Schlieren photographs for the last entry in Table 4. Note that the plume is already very large at 20 μ s. This is a more reactive event than the reactive liquid experiments discussed earlier.

Figure 16. Schlieren photograph for Experiment 090894b of 55% theoretical density Teflon. Frame numbering begins at lower right, then left and up. Frame separation is 10 μ s.

The photographs in Fig. 17 appear to indicate a more timid reaction, but the timing is only a tenth of Fig. 16.

Figure 17. Schlieren photograph for Experiment 081294e with 56% theoretical density Teflon. Frame numbering is the same as Fig. 16, but the time between photographs is only 1 μ s.

The mass spectral data from Experiment 0907094b show rapid appearance of products of the reaction of Teflon. The products arrive quickly, and everything is over by 0.6 ms. Figure 18 shows the temporal traces for four ions. These represent the major product, CF_4 ; remnants of the decomposed Teflon; and ions from the copper slapper. All of these have about the same temporal shape, but those from CF_4 (CF_3^+ and CF_2^+) arrive a bit more quickly than the copper ions or the decomposed Teflon (C_2F_4^+).

Figure 18. Time dependence of four mass spectral signals for Experiment 090794b with 40% theoretical density Teflon. See Fig. 14a. The masses of the ions are, respectively, 69, 50, 63, and 100. All traces are scaled to the same maximum.

Thermodynamic equilibrium calculations indicate that Teflon will decompose by the reaction

with an energy release of about 1 kJ/g. Figure 19 is the result of a spectral assignment from Experiment 090794b. We see that CF_4 is indeed the major product. The other assigned ions are carbon fragments, copper ions, and Teflon fragments.

Figure 19. All of the masses from Experiment 090794b.

Conclusions--Teflon Experiments

The Teflon experiments are only preliminary. They do show, however, that the reaction is violent and that the reaction products are those predicted by equilibrium calculations, carbon and CF₄. Additional experiments will be necessary to better clarify the effect of voids and density on the reaction.