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FINAL REPORT

LIQUID PHASE REACTIONS OF HYPERGOLIC PROPELLANTS

By

S. E. Rodriguez
A. E. Axworthy

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Technical Management
NASA-JET PROPULSION LABORATORY
Pasadena, California
J. Houseman

Rocketdyne
A Division of North American Rockwell
6633 Canoga Avenue, Canoga Park, California

FOREWORD

This report was prepared in compliance with NASA-JPL Contract NAS7-739 entitled "Liquid Phase Reactions of Hypergolic Propellants." Dr. J. Houseman, Jet Propulsion Laboratory, was the Project Manager. The Rocketdyne Program Manager was Mr. T. A. Coultas. The work was carried out by the Physical Chemical Processes group under the direction of Dr. K. H. Mueller. The Principal Investigators were Dr. S. E. Rodriguez and Dr. A. E. Axworthy.

ABSTRACT

Heat and gas release rates were measured for the initial reaction of liquid nitrogen tetroxide with hydrazine, monomethyl hydrazine, and unsymmetric dimethyl hydrazine. A free jet (60^{o}) impingement technique was developed which permitted these rates to be measured for very short reaction times near 100 and 200 microseconds. A very basic quench solution was required to obtain reproducible heats of quenching for the unreacted propellants. High rates of heat and gas release were measured. These were on the order of 10^5 kcal per mol NTO per second and 1000 mol gas per mole NTO per second, respectively. The order of reactivity with NTO was found to increase markedly in the series: hydrazine < UDMH < MMH.

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SUMMARY

Heat and gas release rates were measured for the initial reaction of liquid nitrogen tetroxide (NTO) with hydrazine, monomethyl hydrazine (MMH), and unsymmetric dimethyl hydrazine (UDMH). In the experimental method the liquid propellants were mixed by free jet impingement; a simultaneous free flow of concentrated potassium hydroxide quenching solution stopped the combustion reaction at the periphery of impingement; calorimetric and PVT measurements established total heat and gas release. Combustion time was established by the distance from impingement to quench and the propellant velocities.

Experiments were conducted with combustion times near 100 and 200 microseconds. Quenching tests without direct propellant impingement provided the equivalent of zero combustion time. The propellant jets were 0.028-inch in diameter and were impinging at 60 degrees; average jet velocity was about 80 feet/second; propellants at 50 F were discharged into ambient air.

The heat release rates obtained were 4×10^4 kcal/sec-mol NTO for hydrazine impingement, greater than 20×10^4 for MMH, and about 14×10^4 for UDMH. The gas release rates were 400 mol gas/sec-mol NTO for hydrazine impingement, more than 1200 for MMH, and 900 for UDMH. Measurements on NTO-hydrazine with jet velocities of only 40 feet/second gave about the same heat release rate as for 80 feet/second jet velocities at the same residence times.

The results obtained in this program lead to the following conclusions:

1. The impinging jet technique allows heat and gas evolution rates of hypergolic reaction to be measured at reaction times of 100 microseconds. This is about an order of magnitude lower than the reaction times that were achieved in earlier studies.

2. The heat and gas evolution rates were very high i.e., on the order of 10^5 kcal/sec.-mol NTO and 1000 mol gas/sec.-mol NTO, respectively.

3. The rates observed were relatively independent of reaction time for a given propellant system. They varied by not more than a factor of two for 100 and 200 microseconds reaction.

4. For a given residence time, a variation in jet velocity did not affect the heat evolution rate.

5. The heat and gas evolution rates are definitely dependent on the propellant system. This was found to be the case even though the oxidizer, NTO, was the same in the three systems studied, and the fuels belonged to the same family, i.e., hydrazine, MMH, and UDMH. The MMH/NTO system exhibited the highest heat and gas evolution rates.

INTRODUCTION

The objective of this program was to develop an experimental method for the measurement of heat and gas release rates from hypergolic propellants reacting in the liquid phase. Nitrogen tetroxide-hydrazine was the propellant combination of primary interest. The heat and gas release data relate to jet separation or blow-apart during the mixing of reactive liquid streams. Liquid propellant rocket engine injectors often utilize impinging free jets to provide primary fuel-oxidizer mixing. Under certain conditions, the resulting propellant mixture is not as uniformly distributed as in comparable non-reactive streams but is excessively rich in fuel or oxidizer at either side of impingement. This inefficient mixing is generally ascribed to "blow-apart" of the impinging jet streams as the result of gas generation in the impingement zone. One theoretical model (Ref. 1) to predict the occurrence of blowapart requires the rate of heat release from liquid/liquid reactions in the impingement zone. This heat release rate determines if the propellants will boil within the impingement zone, thereby preventing complete mixing of the streams.*

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* A number of theoretical models have been proposed for the blowapart phenomena (Ref. 2). The data generated under this program are intended to be useful in the further development of these models.

EXPERIMENTAL METHOD

SELECTION OF APPROACH

The experimental approach selected for the program consisted of impinging free jets to mix the propellants and the use of a simultaneous free flowing stream of a quench liquid (coaxial to the fuel jet). The quench stream is employed to stop the reaction at the periphery of the impingement zone and establish the reaction time. Calorimetric and PVT measurements are made to determine gross heat and gas release. This method is similar to that of Refs. 3 and 4 in that a known reaction time is established prior to quenching and the heat release from reaction is obtained by measuring the temperature rise of the quench liquid. However, in the previous work fast mixing of the propellants was accomplished within a reaction tube discharging into a quench liquid (water). In the present case, mixing occurred from free jet impingement. Mixing by free jet impingement was chosen for two reasons. First, the method of mixing may be expected to influence propellant reactivity and jet impingement corresponds to rocket engine practice. Secondly, free-jet mixing facilitates reaching combustion times below 200 microseconds which are not usually attainable with confined-flow reactors. This minimizes boiling and ignition of the propellants.

The significance of the type of heat and gas release rates obtained in this investigation is indicated by the use made of such data in Reference 1. In Reference 1 a heat release per unit time, per unit mass of mixed propellants, within a zone of uniform mixing and reaction formed by propellant impingement is defined. An experimental measurement of this quantity would be generally based on determining the gross heat release from mixing known amounts of liquids, and allowing combustion to proceed for a known time interval. However, the reaction times of interest are very short, on the order of 100 microseconds, corresponding to the residence time of propellants in the impingement zone of typical engine jets. These residence times are comparable to the time scale of mixing processes; in fact, jet impingement is itself intended as a mixing process. Therefore, the experimental approach to measuring such release rates must give special attention to the mixing process used because mixing may be the controlling process.

The two most important aspects of mixing are its configuration and reproducibility.* Combining two propellant flows does not imply instantaneous mixing and reaction throughout the entire mass. Rather, the extent of the mixing and reaction zone will depend on the time elapsed and/or the mixing configuration. The experimental conditions must be chosen so that the propellants are either uniformly mixed or the fraction mixed in the allowed residence time must be reproducible; in the latter case, the residence time can be corrected to some effective value. In regard to the configuration, heat and gas release rates will depend on the extent of liquid intermingling of the multiplicity of propellant contact areas within the reaction zone. For the resultant data to be useful, the experimental mixing process and the mixing process in the intended application must be identical.

The consideration of mixing configuration, i.e., the need to compare and relate the experimental mixing process to the practical case of impinging jets, was the dominant reason for choosing an experiment

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* The reasons that hydrazine and NTO are expected to be imiscible are discussed in Appendix III.

based on impinging free jets. Other possible experimental approaches which departed from this mixing method were considered but were finally discarded.

The most likely alternative approach would generally involve confined propellant flow through an efficient mixing chamber, followed by a length of reaction channel. This mixer-reactor approach is ordinarily utilized in investigations of fast liquid/liquid reaction kinetics; and numerous experimental techniques of this type have been published (e.g., Ref. 8). In such investigations, the objective is to mix as quickly and efficiently as possible, which usually implies a mixing chamber of very small volume with multiple entering streams and/or very turbulent flow. Nearly complete mixing, as judged by the progress of a known reaction, may be obtained in mixing times of hundreds of microseconds; but the mixing times are generally longer than the reaction times of interest and the experimental results require extrapolation back to initial contact. In comparison with free jet impingement, a confined-flow mixer-reactor experiment would probably yield more precise results if complete mixing could be obtained.

As mentioned previously, a mixer reactor had been used elsewhere for heat and gas release measurements on hypergolic liquids (Refs. 3, 4). The mixer was a four-jet chamber and the relation between this experiment and impinging free jets in a rocket engine was left open to question. Some of the problems associated with the reaction tube method used in References 3 and 4 may be seen from the following analysis. The total heat evolved by propellant reaction (excluding the heat of quenching) ranged from 0.1 to 1.5 kcal in each of the previous experiments. Since only two ml of liquid propellants was used in each experiment, the heat required to bring the propellant mixture to its bubble point (Ref. 1) is less than 0.02 kcal. It is apparent that most of the measured heat release resulted from reactions of propellant vapor. In fact, it can be shown that for 2.5 grams of reaction products (and unreacted propellants) to contain this energy, the average temperature must have been in excess of 1000^{0} C in some of the experiments. It is apparent, therefore, that the propellants must have ignited in the reaction tube or continued to react for some time after leaving the tube before becoming intimately mixed with the quench liquid.

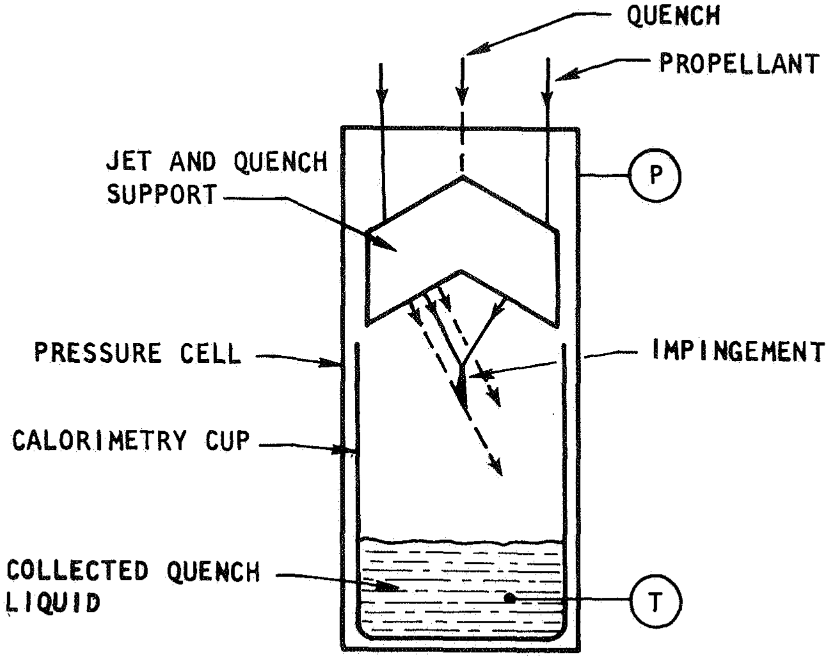
The main problem with the reaction tube method appears to be that the hypergolic reactions to be studied are so fast that the minimum attainable reaction times are too long to prevent ignition. The theoretical reaction times for the apparatus used in References 3 and 4 are in the range of 500 to 1500 microseconds. It was shown in Reference 1, however, that the propellant mixture will reach its boiling point in less than 50 microseconds (provided that the heat release rate is that reported in Ref. 3). In addition, the volumes of the tube reactors (0.5 to 1.7 ml) were on the same order as the volume of liquid propellant used. There is a good chance, therefore, that some of the propellant may have remained in the reactors for times much longer than the calculated residence times. For these reasons a reaction tube experiment was not used here.

APPARATUS AND PROCEDURE

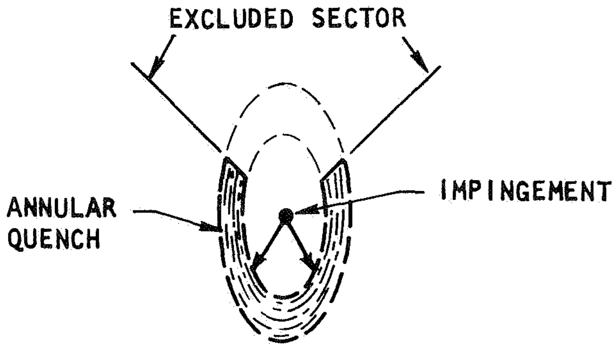
General Procedure

The experimental arrangement is shown in Figures 1, 2, and 3. Figure 1a shows the support block which holds the propellant feed tubing and a nozzle for the discharge of quench liquid. The propellant jets impinge at an angle of 60 degrees. Simultaneously, an annular free stream of quench liquid is discharged concentrically with the fuel jet. Figure 1b shows the conditions in the impingement plane, i.e., the central plane for the outflow of mixed propellants. The section

SCHEMATIC OF IMPINGEMENT APPARATUS



(a) EXPERIMENTAL ARRANGEMENT



(b) IMPINGEMENT PLANE

Fig. 1. Schematic of Impingement Apparatus

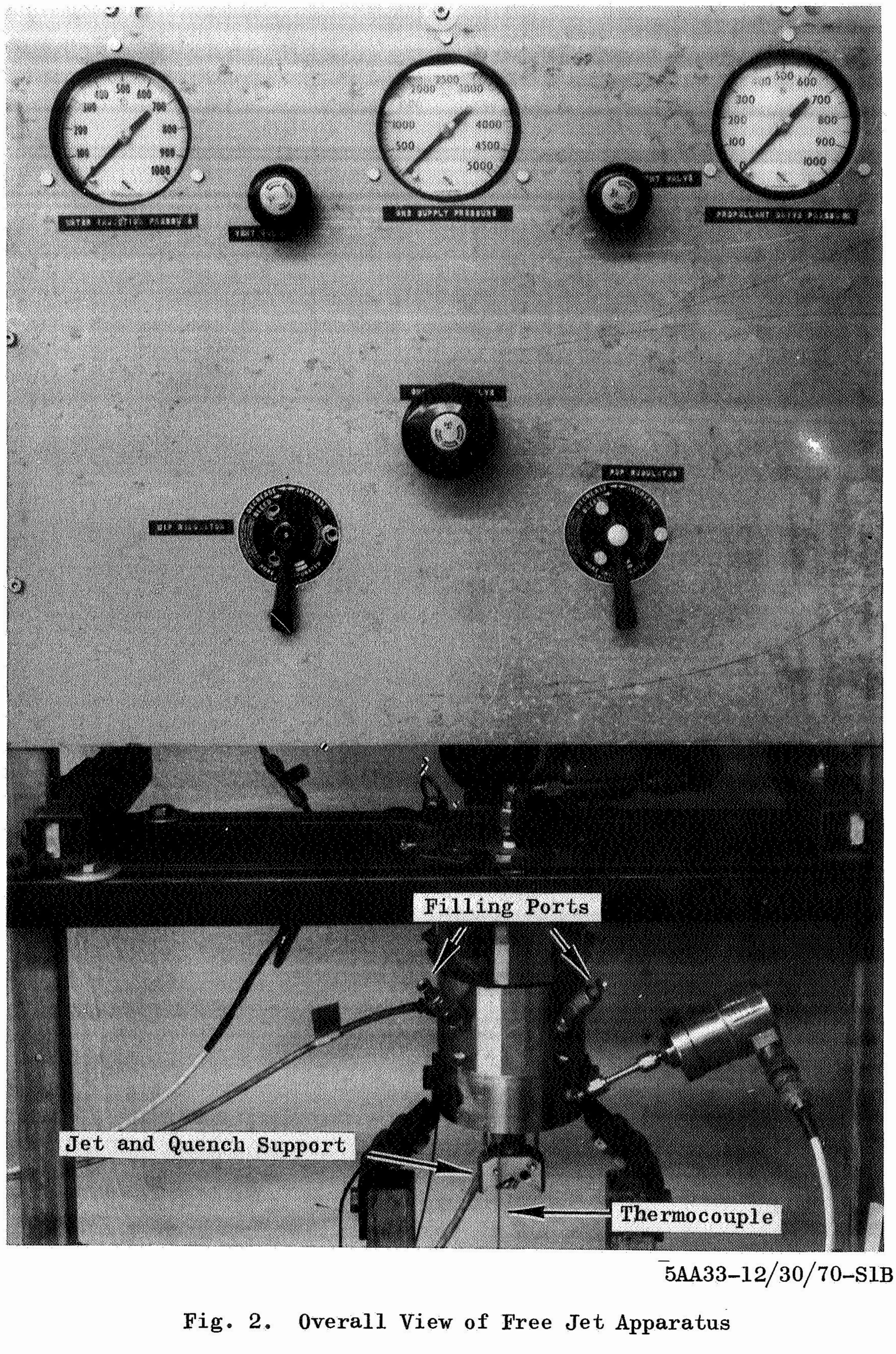


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Fig. 2. Overall View of Free Jet Apparatus

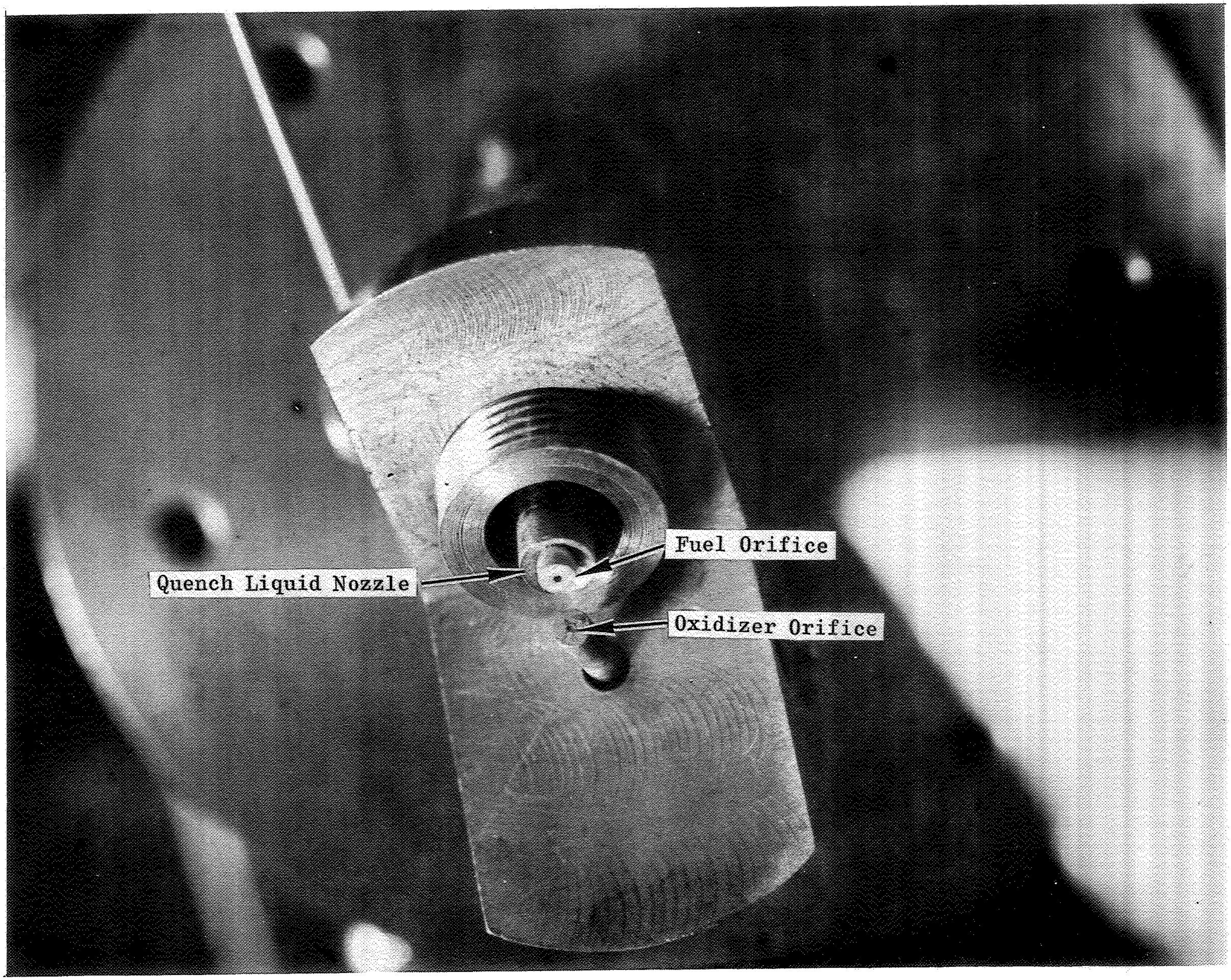

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Fig. 3. Propellant Orifices and Quench Nozzle

of the annular quench stream crossing the impingement plane is elliptical because of the 60-degree impingement angle. A sector of the annular quench flow was eliminated at the back of the impingement zone to prevent the quench stream from interfering with the opposite jet. After impingement, the propellants travel outward undergoing combustion until they enter the quench stream, where rapid dilution and a quenching reaction takes place. Figures 2 and 3 show the overall view of the apparatus and the orifice and quench arrangement, respectively.

In a typical experiment, the propellant and quench flows are maintained for a sufficiently long time to represent steady-state impingement. The quench liquid is collected within a plastic cup in the experimental cell. The temperature rise of the quench liquid is measured to establish total heat release. The pressure rise within the cell is measured for PVT calculation of the gas release. After suitable data reduction, an experiment yields the total heat and gas evolved per unit mass of propellants injected. The heat and gas release due to the quenching reaction are determined from a separate experiment. To arrive at specific heat and gas release from combustion, the fraction of injected propellants which has actually been mixed at impingement must be determined in some manner or assumed to be unity, i.e., complete stream mixing. The latter was assumed here. To obtain rates of heat or gas release, the combustion time prior to quenching must be determined. This combustion time was established by the inner diameter of the annular quench stream and the exit velocity of the propellants mixture (see results section of this report).

Propellant Expulsion

The propellant expulsion system was the same used by prior investigators (References 3, 4) and supplied by NASA-JPL for this program. In this system, the propellants contained in four cylinders were simultaneously expelled by pistons pushed by a single larger gas-driven piston. Propellant flow was started by rupture of thin Teflon sheet discs sealing the cylinder outlets. The four propellant cylinders were originally bored with different diameters to allow for many mixture ratio variations. For the jet doublet experiment these four cylinders were combined as two pairs, one for each propellant. The pairing was accomplished by suitable passages in a specially constructed flange which connected the expulsion unit to the propellant jet feed tubing. However, there resulted only four possible propellant volume ratios.

Propellant expulsion was initiated by the opening of a timer-controlled solenoid valve which allowed nitrogen gas at a regulated pressure to act on the drive piston. The drive pressure, typically 500 psia, determined the resultant rate of discharge. Propellant discharge ended when the drive piston bottomed out against the propellants cylinder flange. The time of discharge was measured in order to calculate jet velocities. For this measurement, the core of a linearly variable differential transformer was attached to the drive piston, the transformer signal was displayed on an oscilloscope and photographed during expulsion. A reasonably linear trace of piston travel against time was obtained, although it typically showed irregular behavior and relatively higher velocities for the start of expulsion. This feature may have resulted from various factors: compression of ullage gas in the propellant cylinder, fill of the propellant passages, and/or slightly different delays in rupturing the cylinder outlet seals. The estimate of overall expulsion time has an approximate error of five percent. Expulsion times were typically between 0.10 and 0.15 sec, except for a set of low velocity measurements with about twice the duration. The titles and Rocketdyne numbers of equipment drawings are shown in Table I.

TABLE I. EQUIPMENT DRAWINGS

Title	Rocketdyne No.
Flow Cylinder, Free Jet Reactor	R6D6360
Flow Controller, Free Jet Reactor	R6D6361
Flow Controller Cap, Free Jet Reactor	R6D6362
Water Flow Fitting, Free Jet Reactor	R6C6363
Flow Adjustor, Free Jet Reactor	R6C6364
Tube Adjusting Screw, Free Jet Reactor	R6C6365
Piston Rod No. 3, Free Jet Reactor	R6C6366
Piston Rod No. 4, Free Jet Reactor	R6C6367

Propellant Volumes

The propellant volumes discharged were about one cc oxidizer in each case and, 1.20, 1.35, and 1.35 cc of hydrazine, MMH, or UDMH, respectively. The volumes were determined from the known propellant cylinder areas and cathetometer readings of the distance traveled by the large piston. A volume correction of about 0.1 cc was made for propellant holdup in the connecting flange passageways and jet feed lines. These flow channels were partially blocked with wire both to reduce the volume correction, and to increase flow resistance, which improved the reproducibility of the expulsion rate. An effort was made to discharge about the same volume in all tests to improve the experimental precision. Difficulties in setting the initial piston position led to an overall range of about 20% in the discharged volume, but this variation did not seem to affect the specific results.

The calculation of propellant volumes assumed that the propellant cylinders were completely filled and discharged through the jets without leakage. Loading of the propellant cylinders was accomplished in two steps: first the atmospheric pressure prefill chamber associated with each cylinder was filled through long tubing reaching to the bottom of the chamber, seeking to exclude all air; second, liquid was drawn from the prefill chamber into the cylinder by raising the piston. Water tests were performed to check this filling operation and the volumetric discharge of the cylinders. These tests indicated that the liquid volume actually discharged could be as much as ten percent less than calculated. The deficiency was most likely due to transfer of air bubbles into the propellant cylinders during filling. In addition to this possible loading error, the high cylinder pressure developed at discharge could cause leakage past the propellant piston o-rings and the valve-type closure on the orifice connecting to the fill chamber. Precautions were taken to minimize these loading and leakage effects but perhaps several percent error in the estimate of propellant quantities, and a corresponding lack of precision still remained.

Propellant Temperature

In all the tests conducted, the propellants were expelled at about 50°F. Chilling was required to load liquid nitrogen tetroxide (NTO) because the fill chambers of the expulsion unit could not be pressurized and the NTO boiled at ambient conditions. Moreover, since the propellants were discharged into ambient pressure, a temperature range below boiling helps to prevent blowapart by NTO boiling in the impingement zone (Reference 1). For chilling, a dry-ice bath was put in contact with the propellant cylinder flange prior to assembling the drive piston unit. The temperature was measured by a thermocouple in a well located among the propellant cylinders.

Propellant Jets

In all tests conducted, both propellant jets were 0.028 inch in diameter. Relatively small propellant jets were desirable for two reasons: diminished likelihood of blowapart (References 1, 5, 6, 7) and better definition of the impingement center location and the distance to quench.

The jet feed lines were 1/8-inch O.D. stainless steel tubing with a smooth exit orifice. The support block allowed a straight run of about 1.5 inches before the orifice. Free flow distance to impingement was about 1/8 inch. The jets were aligned by visual observation of water flows. Periodic checks indicated that alignment was not impaired by repeated testing.

The 60-degree jet impingement posed some special problems. The outward mass flux of the propellant mixture is not uniform but is concentrated in the direction of the resultant momentum (downwards in Figure 1b), and the quenching radius is not uniform but elliptical in the impingement plane. The effective quench distance is therefore an average, weighted according to the mass flux distribution. More importantly, a portion of the quench stream had to be removed in order to protect the opposite jet stream. These geometrical problems could have been avoided with directly opposed jets. However, the 60-degree impingement has greater practical significance and has received more experimental attention. The angle was also experimentally advantageous in that the quench stream could be directed away from the support hardware, thus helping to reduce splashing and calorimetric error.

Quench Liquid

The quench liquid used for all the reported data was approximately 3-molar potassium hydroxide solution. Since both the combustion and quenching reactions contribute to the total heat and gas evolution, the quench reaction contribution must be reasonably invariant. Lengthy initial experimentation with a plain water quench showed that the heat release from NTO and hydrazine reacting in water solution depended on the mixing processes with the water. Although attempts were made to standardize the quench velocity and the initial dilution process, no meaningful data were obtained with the plain water quench.

Therefore, a special theoretical and experimental investigation of the NTO-hydrazine quenching reaction was conducted, leading ultimately to the concentrated KOH quench solution. This investigation is reported in detail in Appendix I. Apparently, some of the nitrous acid which, along with nitric acid, results from NTO solution, can decompose or react directly with hydrazine before being neutralized. Hence, the neutral water quench reaction can vary and quench heat release is sensitive to the propellant/water mixing process. A caustic quench solution can eliminate or reduce this variability because both nitrous acid decomposition and the direct reaction of nitrous acid with hydrazine are acid catalized, and because the high hydroxide ion concentration promotes simple neutralization of the nitrous acid. Variable quench behavior did not occur with the concentrated KOH solution, at least within the experimental accuracy. Experiments with different quench flow rates which were known to yield substantially different heat results with neutral water gave consistent results with the KOH solution.

Quench Flow

Quench liquid was discharged by actuating a fast valve between a pressurized tank containing an excess of liquid and a short flow line to the quench nozzle. A timer operated the quench flow valve as well as the valve supplying high pressure gas to the propellant expulsion unit. The experiment requires that the quench flow be present in the impingement plane during propellant injection. To insure this condition (and to avoid excessive quench stream velocities) the quench flow time was relatively long, from one-half to one second. Quench liquid volumes of about 150 to 200 cc were discharged at velocities of about 10 to 30 feet/sec.

Two sizes of impingement quench nozzle were utilized: 1/8-inch I.D. with 3/8-inch O.D. in which the jet tubing itself gave the I.D.; and 1/4-inch I.D. with 7/16-inch O.D. using a sleeve over the jet tubing. A rubber plug in these annular nozzles blocked off about one-third or one-quarter of the area in order to exclude flow from the back of the impingement zone, as shown in Figure 1b. With smooth, full flow in the nozzle and reasonably high velocity, the free stream internal diameter was a well defined extension of the nozzle internal diameter, at least over the free flow distance of about 1/4 inch to the impingement plane. Nozzle performance was checked with water flows, but only visually. Propellant impingement experiments repeated with different nozzles having the same dimensions, and varying quench flow rates showed satisfactory reproducibility.

Temperature and Pressure

In the original experimental design, quench liquid temperature and cell pressure measurements were to be taken in each test, as indicated by Figure 1a. However, in initial experiments, significant spilling of quench liquid from the plastic calorimetry cup could not be prevented. The principal problem was that the cell had a small (about 550 cc) volume (to increase pressure response) and could not hold a sufficiently large cup. Ultimately, heat and gas release tests were conducted separately; the heat tests with a large open plastic cup which could collect the quench stream, and the gas tests with the pressure cell. Heat release testing with a translucent cup had the advantage that light and sound emission due to combustion could be observed.

The temperature rise in the discharged quench liquid was recorded directly as the voltage difference of two copper-constantan fast-response thermocouples located respectively within the calorimetric cup and within the quench liquid tank. The quench liquid tank was at ambient temperature; special tests showed that, after allowing proper temperature equilibration, discharging the quench did not affect the tank liquid temperature significantly. In a typical test, the cup thermocouple showed a fast initial temperature rise, sometimes a spike, followed by a slower equilibration which presumably resulted from temperature equilibration in the liquid and/or residual heat of solution effects. The quench liquid was stirred in the calorimetry cup to speed up the equilibration. A stabilized temperature rise, typically 10^{o}F or less, was obtained within seconds after the discharge. Heat loss from the plastic cup, which was warmed prior to testing was relatively slow and did not require major correction. The temperature rise did include a small temperature change caused by friction and heat transfer in the quench injection line. This temperature correction, less than one degree Fahrenheit, was obtained by repeating the quench injection, but without propellants, shortly after each test.

In the gas release experiments, the pressure rise in the cell was measured with a strain gauge type pressure transducer. Initially, the cell held ambient atmospheric pressure (about 13.7 psia). The typical test pressure behavior consisted of a fast initial rise followed by a slower decay toward equilibrium, which occurred a few minutes after propellant discharge. The final pressure increase was around 10 psi. The calculated gas release was corrected for the volume occupied by the quench water.

RESULTS

EXPERIMENTAL PARAMETERS AND ASSUMPTIONS

Heat and Gas Release

For each propellant combination investigated, experiments were conducted with an approximately fixed mixture ratio and variable allowed combustion time. The increase of the total heat or gas released per mol oxidizer as a function of combustion time yields the rate of release. Total heat release was obtained from the corrected temperature rise and the mass and heat capacity of the quench liquid injected. Total gas release was obtained from the cell pressure rise, gas volume, and temperature; the perfect gas law was assumed to hold. Gas products were not analyzed and no corrections were made for possible post-quench gas reactions or solution of gas products in the quench liquid. Heat and gas release were calculated on the basis of total NTO discharged, which assumes, in all cases, that the propellants participated uniformly in combustion, i.e., that there was complete stream mixing and blowapart did not occur.

Combustion Time

The inner diameter of the annular quench stream and the propellant exit velocities establish the combustion time prior to quenching. For the data presented below, combustion time was estimated by the formula $t_{comb.} = 0.75\ D/V$, where D is the inner diameter of the quench nozzle and V is the average velocity of the propellant jets. Here three basic assumptions are made: (1) the inner diameter of the free quench stream is identical to the inner diameter of the quench nozzle, (2) the exit velocities are equal to the average velocities of the propellants, and (3) from flow momentum considerations, the mass flow of the mixture in the impingement plane is concentrated towards elliptical radii at 30 degrees from the impingement axis, as indicated in Figure 1B. The approximation neglects a number of lower order factors determining the effective combustion time. Among these are: velocity decay due to turbulence in the approach and exit propellant flows; the finite size of the impingement zone, which implies a shorter effective quench distance; the precise distribution of outflow in and about the impingement plane; the small fraction of outflow unquenched at the back of impingement; and the effect of gaseous reaction products on outflow velocity. These factors could contribute a substantial absolute error, possibly as high as 25 percent to the estimate of combustion time. However, the overall experimental intent and the experimental accuracy did not warrant taking into account the above factors.

Combustion time was primarily varied by means of the quench I.D. Except for a special set of tests conducted with hydrazine, the average jet velocity was always near 80 ft/sec. This velocity gave combustion times of about 100 microseconds, and is typical of practical rocket engine injector jet velocities. Jet velocities were estimated from the propellant volumes discharged, the time for discharge, and the jet orifice area. The jet velocity estimates were probably within 10 percent; the quench diameter estimates within twenty percent. The latter figure is derived from the reproducibility of tests with hydrazine involving several quench nozzles having the same dimensions.

Quenching Only

Data were obtained for zero combustion time by allowing the propellant jets to enter the quench stream directly, instead of after impingement. The experimental arrangement for quenching only was similar to that for impingement, but the partial quench nozzle plug was removed so that the quench stream intersected the opposite jet stream. In most quenching only experiments, the end of the jet tube within the quench stream was rounded, which tended to direct the quench into the enclosed jet stream, and the jets were deliberately misaligned. Comparisons indicated that these two precautions had no significant effect on the results of quenching.

The data for repetitive quenching experiments provide a useful indication of the experimental precision. Except for the variables which establish combustion time, and the combustion process itself, the reproducibility of quenching alone indicates the effects of all other procedural and physical factors. These include volumetric and leakage errors in the amounts of propellants discharged, errors in the measurement and correction of temperature and pressure rise, and variability of the quench reaction path. Hence, lesser reproducibility in an impingement-combustion experiment is generally indicative of combustion process variability. In particular, quenching only tests with different quench discharge rates indicate whether the propellant/quench mixing process can affect the results. Tests of this type led to the rejection of water quenching, as discussed previously.

Quenching Assumptions

Equating heat release from quenching alone to that for zero combustion time implies that quenching alone corresponds to the quenching of mixed propellants around the impingement zone. This assumption is reasonable if the time required for the mixture to dissolve in the quench stream is short compared to the combustion time.

Reasonable consistency was obtained in combustion experiments with different quench discharge rates. Since the latter should affect the speed of initial solution, the results indicate that the time required for solution of the propellants did not significantly affect the experimental accuracy.

Deriving rates of heat and gas release from the slope of total release against combustion time implies that the quench reaction contribution is constant. This cannot be generally true; with increasing combustion time less of the original propellants are quenched. The heat or gas release from quenching may not be properly assumed constant unless it is small in relation to the combustion release. This was true for the gas release data obtained. The heat of quenching, however, was not negligible in comparison to the heat of combustion. Hence, Δheat release/Δtime slopes generally give a low estimate of combustion heat release rate. A correction for the change in the amount of propellant which is quenched would require postulating specific combustion reactions with known heats of reaction as discussed in Appendix II. No correction was made for this effect.

DATA

Heat and gas release data were obtained for nitrogen tetroxide (NTO) impinging on hydrazine, monomethyl hydrazine (MMH), or unsymmetric dimethyl hydrazine (UDMH). Propellant jets were 0.028-inch diameter impinging at a 60° angle; propellants at 50° F were discharged into ambient air at about 70° F and 13.7 psia. The calculated heat and gas release values are reported to three significant places and the calculated combustion times to two places. However, the last places are not significant in view of the experimental uncertainties. The tables also give the amounts and flowrates of quench liquid and the volume and velocity of the oxidizer; the corresponding fuel volumes and velocity are in proportion to the volume ratios given in the text for each fuel.

Hydrazine-NTO

Figures 4 and 5 and Tables II and III show the heat and gas release data obtained for hydrazine-NTO. The oxidizer/fuel mass ratio was about 1.20, and the volume ratio about 0.83. With equal diameter jets, this mixture gave approximately matched jet-stream momenta and optimal mixing. The quenching only results agree reasonably well with theoretical estimates of about 38 kcal/mol NTO and zero mol gas/mol NTO for the quenching reactions in caustic solution (Appendix I).

The heat release points near 100 microseconds reaction time were obtained with four different build-ups of the 1/8-inch I.D. quench nozzles. Examination of these data shows that nozzle variations contributed little to the overall spread, thus indicating that the method of establishing the free quench stream I.D. is satisfactory. The heat release points near 200 microseconds correspond to two different combinations of quench diameter and jet velocities. Although the velocities differed by a factor of nearly two, the two sets of data show reasonable agreement. This result indicates that, for these particular propellant impingement conditions (small diameter jets), jet velocity does not have a large influence on mixing and reactivity. In a few of the heat release experiments near 100 microseconds combustion and in all those near 200 microseconds, there was visible light from the combustion zone.

MMH-NTO

Figures 6 and 7 and Tables IV and V show the heat and gas release obtained for MMH-NTO impingement. The heat and gas release rates were much higher than with hydrazine. The oxidizer fuel mass ratio was about 1.22, the volume ratio about 0.74. For equal jet diameters, this mixture ratio does not give matched momenta, or optimal mixing,

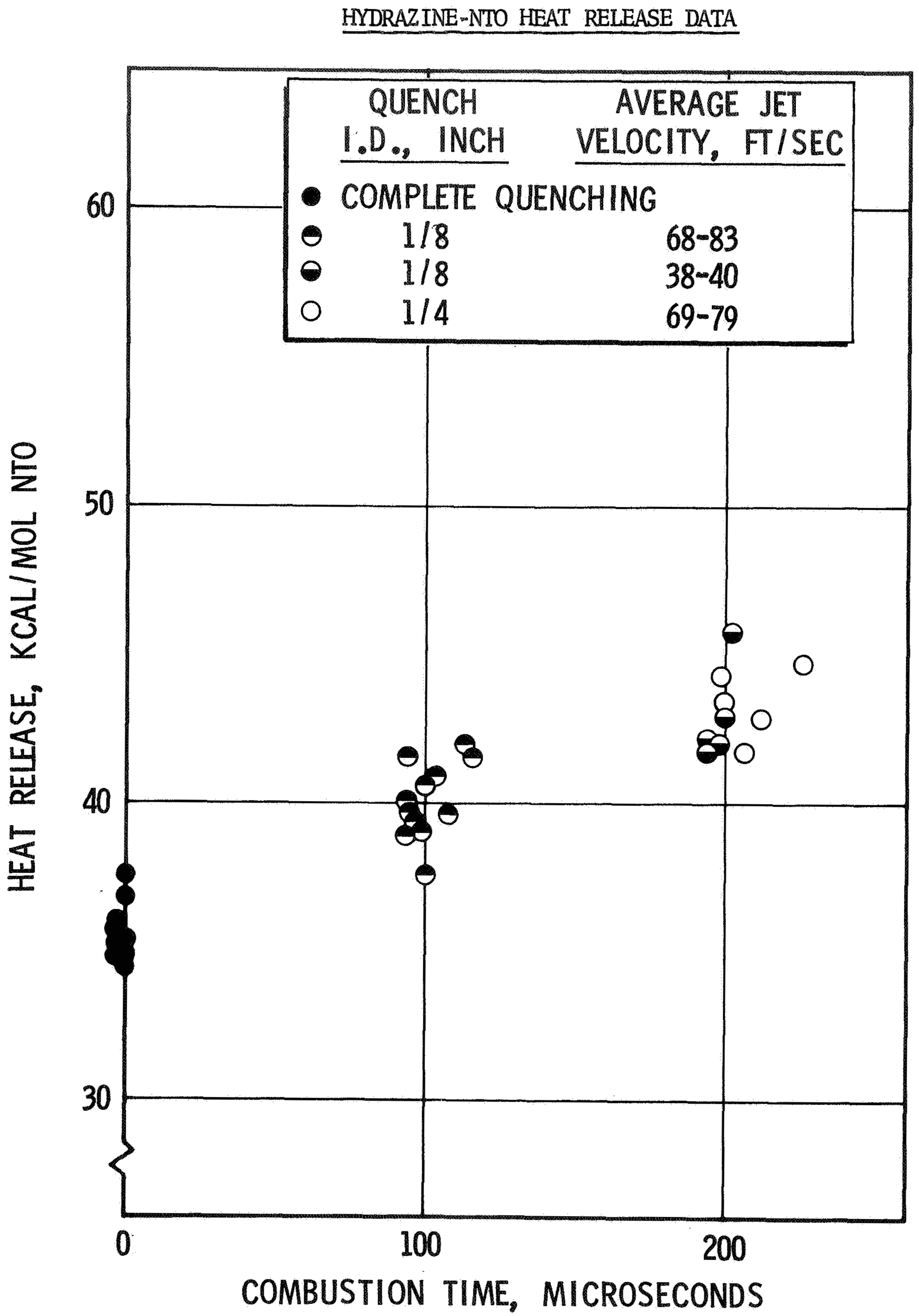

Fig. 4. Hydrazine-NTO Heat Release Data

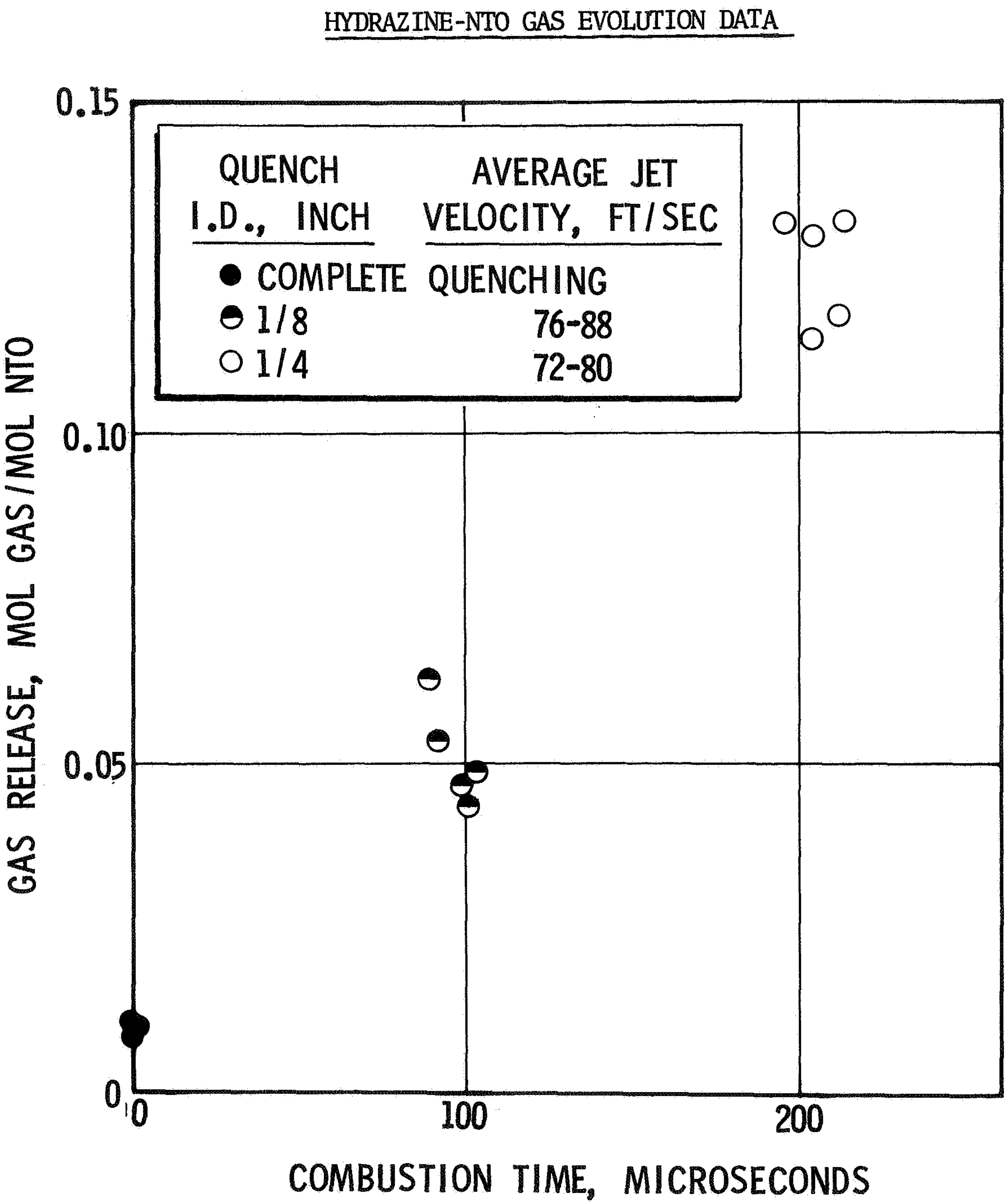

Fig. 5. Hydrazine-NTO Gas Evolution Data

TABLE II. HYDRAZINE-NTO HEAT RELEASE

KOH Quench		NTO		Combustion	Heat
Mass (gm)	Rate (gm/sec)	Volume (cc)	Velocity (ft/sec)	Time (microsec)	Release (kcal/mol NTO)
Complete quench nozzle No. 1					
158	158	1.05	72		34.6
149	447	1.05	69		34.9
160	160	1.07	69		35.4
151	453	1.01	70		36.9
158	158	1.04	69		37.6
Complete quench nozzle No. 3					
199	266	1.01	74		34.9
197	262	0.99	72		35.4
198	264	0.93	74		35.7
197	262	1.09	74		36.0
1/8-in I.D., 3/8-in O.D. impingement quench nozzle No. 1					
168	187	1.06	72	99	37.6
159	318	1.08	76	94	39.0
167	167	1.10	72	99	39.0
157	262	1.07	73	98	39.2
171	228	1.04	73	98	39.5
1/8-in I.D., 3/8-in O.D. impingement quench nozzle No. 2					
198	264	1.02	71	100	40.6
198	264	1.03	62	115	41.8
195	260	0.98	63	114	41.9
1/8-in I.D., 3/8-in O.D. impingement quench nozzle No. 3					
196	262	1.08	65	109	39.6
194	258	1.04	75	94	40.1
195	260	1.02	75	94	41.6
196	262	1.00	37	194	41.8
194	258	1.02	36	198	42.1
196	262	1.02	37	194	42.2
195	260	1.02	35	200	42.9
196	262	1.01	35	202	45.8

TABLE II. HYDRAZINE-NTO HEAT RELEASE (CONT'D.)

KOH Quench		NTO		Combustion	Heat
Mass (gm)	Rate (gm/sec)	Volume (cc)	Velocity (ft/sec)	Time (microsec)	Release (kcal/mol NTO)
1/8-in I.D., 3/8-in O.D. impingement quench nozzle No. 4					
172	230	1.03	68	104	40.9
1/4-in I.D. 7/16-in O.D. impingement quench nozzle No. 1					
178	178	1.03	69	206	41.8
178	324	1.09	67	212	42.9
172	230	1.10	71	200	43.5
195	300	1.04	72	198	44.3
150	200	1.04	63	226	44.8

TABLE III. HYDRAZINE-NTO GAS RELEASE

KOH Quench		NTO		Combustion	Gas
Volume (cc)	Rate (cc/sec)	Volume (cc)	Velocity (ft/sec)	Time (microsec)	Release (mol gas/mol NTO)
Complete quenching nozzle No. 4					
166	249	1.01	67		0.009
162	243	1.04	78		0.010
164	246	0.90	69		0.011
1/8-in I.D., 3/8-in O.D. impingement quench nozzle No. 3					
159	238	1.00	70	101	0.043
161	242	1.02	72	99	0.047
157	236	0.99	69	103	0.049
159	238	1.05	78	92	0.054
157	236	1.01	80	89	0.063
1/4-in I.D., 7/16-in O.D. impingement quench nozzle No. 2					
175	233	0.90	69	204	0.114
174	232	0.86	67	212	0.118
165	220	1.04	70	204	0.130
167	223	0.98	66	214	0.132
129	194	1.07	73	196	0.132

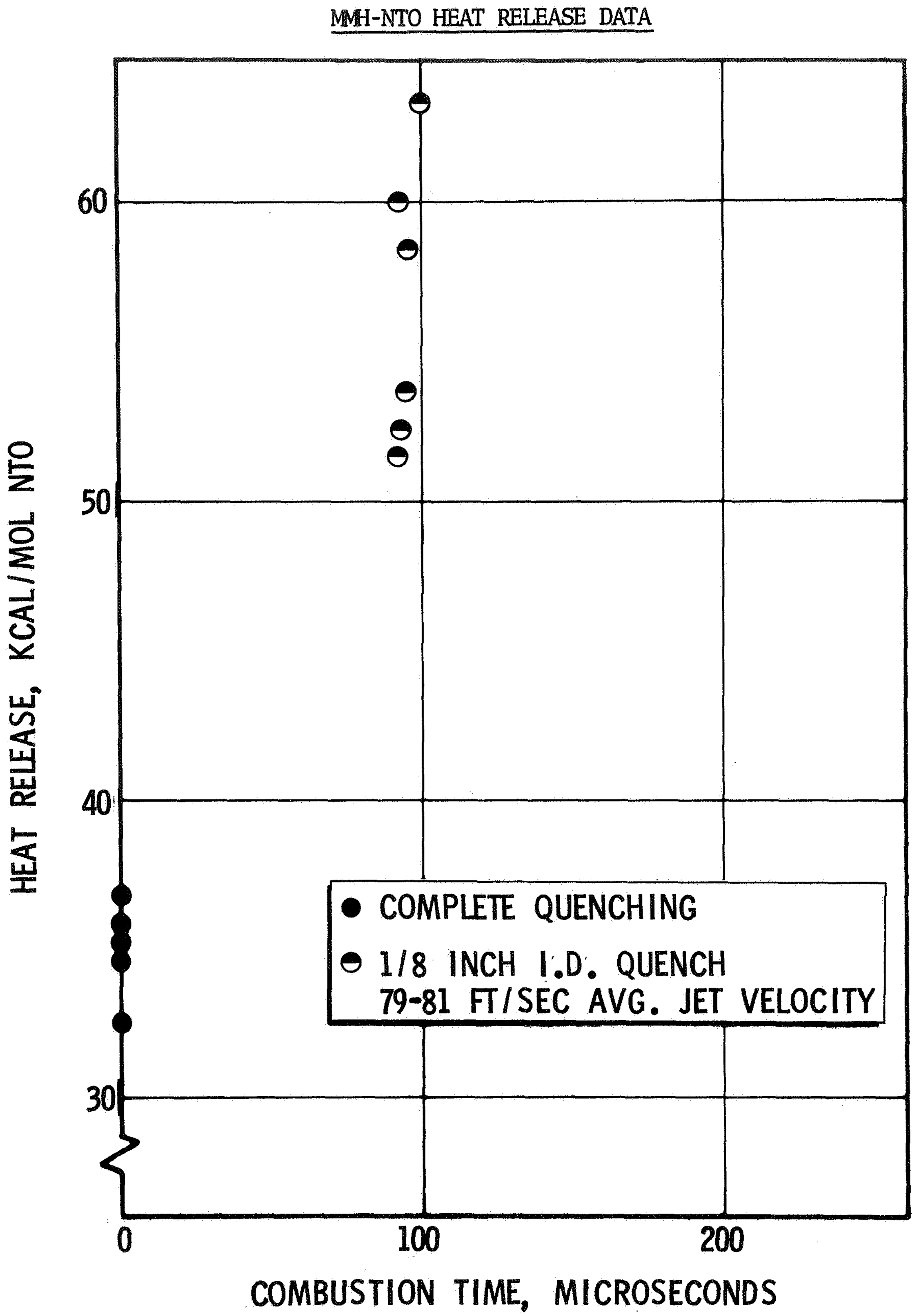

Fig. 6. MMH-NTO Heat Release Data

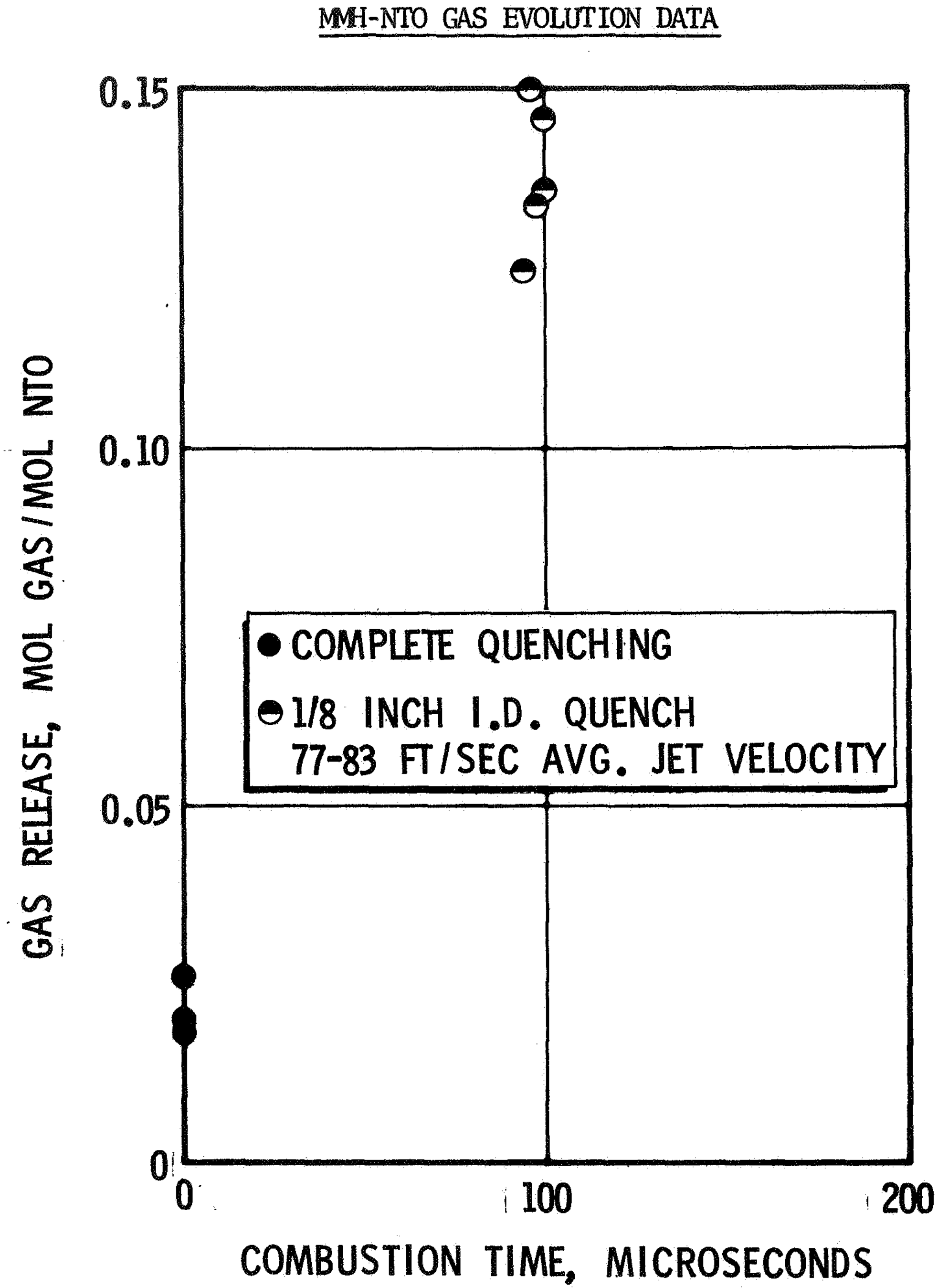

Fig. 7. MMH-NTO Gas Evolution Data

TABLE IV. MMH-NTO HEAT RELEASE

KOH Quench		NTO		Combustion Time (microsec)	Heat Release (kcal/mol NTO)
Mass (gm)	Rate (gm/sec)	Volume (cc)	Velocity (ft/sec)		
Complete quenching nozzle No. 4					
153	263	1.02	66		32.5
200	267	1.04	76		34.6
190	190	0.94			35.2
186	372	0.97	69		35.8
174	261	1.01	67		36.8
1/8-in I.D., 3/8-in O.D. impingement quench nozzle No. 4					
194	258	1.08	71	93	51.5
192	256	0.96	70	94	52.4
194	258	1.01	70	95	53.7
193	350	1.07	69	96	58.4
212	364	1.02	72	93	60.0
196	392	0.98	66	100	63.3

TABLE V. MMH-NTO GAS RELEASE

KOH Quench		NTO		Combustion	Gas
Volume (cc)	Rate (cc/sec)	Volume (cc)	Velocity (ft/sec)	Time (microsec)	Release (mol gas/mol NTO)
Complete quenching nozzle No. 4					
166	248	1.01	66		0.018
162	243	1.02			0.020
163	244	0.98			0.026
1/8-in I.D., 3/8-in O.D. impingement quench nozzle No. 4					
133	177	1.03	70	95	0.125
185	202	0.85	67	98	0.134
171	186	0.98	66	100	0.136
160	174	1.07	67	100	0.146
144	173	1.01	68	97	0.150

but was the closest available in the expulsion unit. The small deviation from matched momenta did not warrant a correction in the estimate of combustion time.

Of the six heat release points, all obtained near 100 microseconds combustion time, the three higher values were obtained with a quench flow rate about forty percent faster than that for the three lower values. This apparent sensitivity to the quench flow rate, which was not observed during quenching only nor in any of the hydrazine tests, indicates that the energetic combustion was disturbing the nominal quench performance in some manner. Possibly, high local heat release in the quench stream caused significant vaporization, or high combustion gas release disrupted the quench stream. Therefore, the heat release measurements are probably low, and their overall spread is not representative of the combustion process.

These combustion heat measurements gave bright light emission and a rasping noise. The effect of quench flow rate was not investigated in the gas release experiments.

UDMH-NTO

Figures 8 and 9 and Tables VI and VII show the heat and gas release obtained for UDMH-NTO impingement. The oxidizer/fuel mass ratio was about 1.35, and the volume ratio about 0.74. This mixture ratio gave matched jet momenta and optimal mixing. The relatively large spread in the heat and gas release values at about 100 microseconds reaction time appears to be a real consequence of variations in the combustion process. In the 100 microsecond heat release measurements there was no evident correlation of results with the quench flow rate, which was varied by a factor of two. For the measurements near 200 microseconds, however, higher quench flow rates tended to yield higher heat

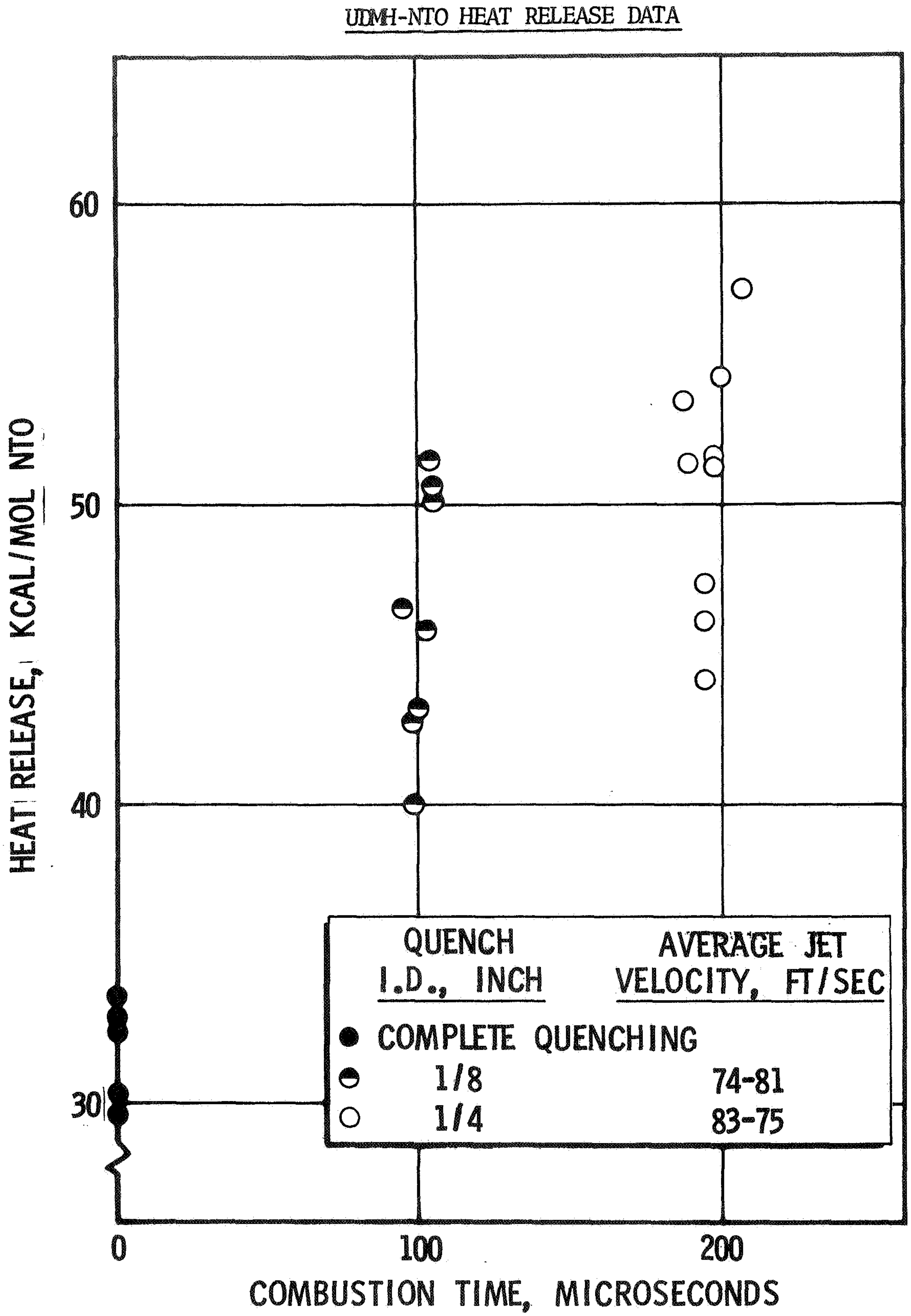

Fig. 8. UDMH-NTO Heat Release Data

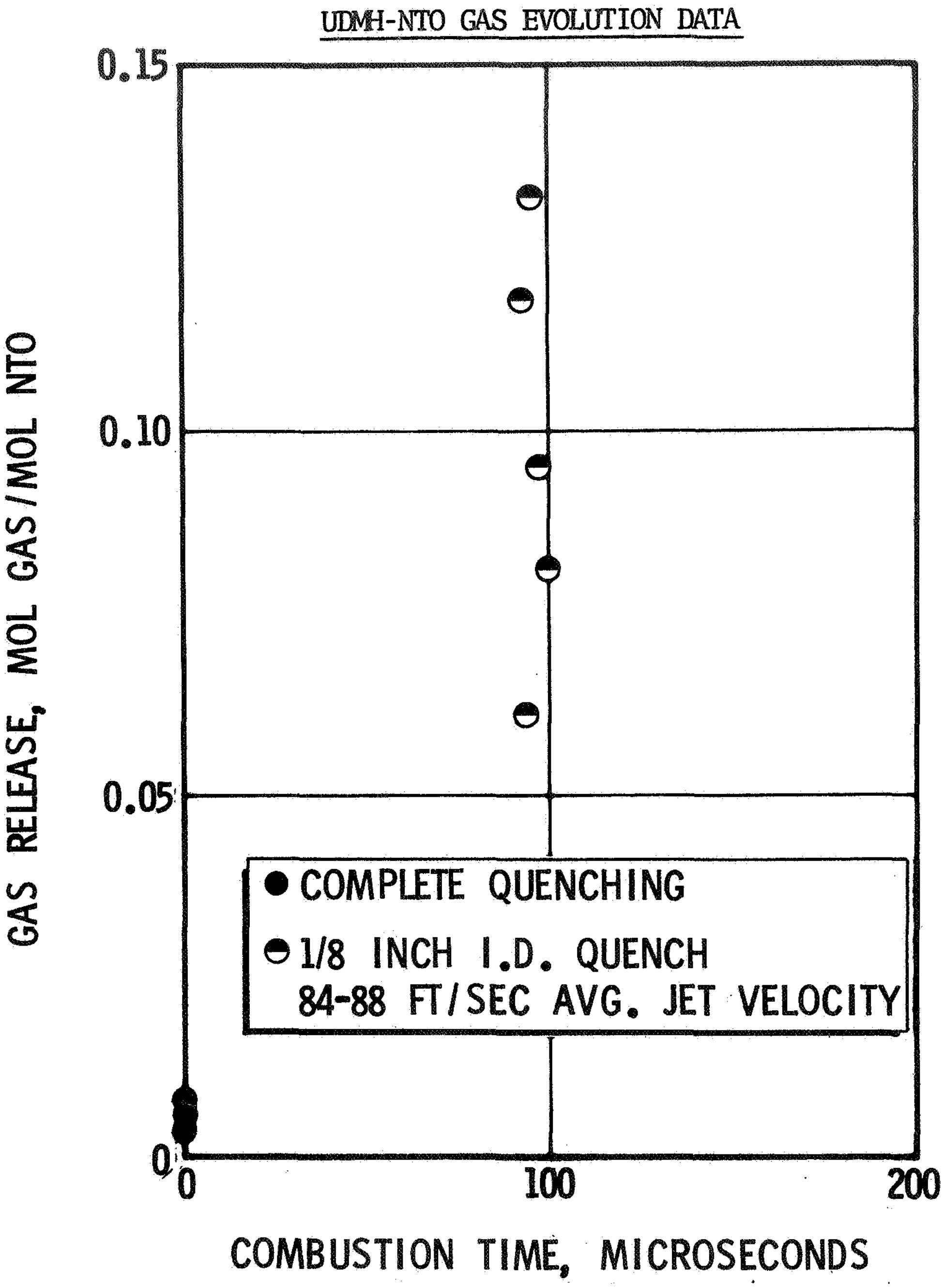

Fig. 9. UDMH-NTO Gas Evolution Data

TABLE VI. UDMH-NTO HEAT RELEASE

KOH Quench		NTO		Combustion	Heat
Mass (gm)	Rate (gm/sec)	Volume (cc)	Velocity (ft/sec)	Time (microsec)	Release (kcal/mol NTO)
Complete quenching nozzle No. 2					
184	184	1.02	70		29.6
182	364	1.10	72		30.0
181	362	0.99	70		31.6
197	262	1.06	69		32.4
197	262	0.99	66		32.9
184	184	0.98	69		33.5
1/8-in I.D., 3/8-in O.D. impingement quench nozzle No. 2					
198	264	1.02	67	99	40.0
184	368	1.06	67	99	42.9
187	187	1.04	67	99	43.2
184	184	0.99	64	104	45.8
176	352	0.99	69	95	46.6
195	260	0.85	63	106	50.2
196	262	1.04	64	104	50.6
195	260	1.01	64	104	51.5
1/4-in I.D., 7/16-in O.D. impingement quench nozzle No. 1					
188	188	1.05	68	195	44.2
207	188	1.04	68	195	46.1
198	264	1.04	68	195	47.4
200	267	0.97	67	198	51.4
187	374	1.02	70	190	51.4
202	270	1.02	67	198	51.6
185	370	1.04	71	188	53.5
200	364	1.04	66	200	54.2
209	380	0.91	64	208	57.1

TABLE VII. UDMH-NTO GAS RELEASE

KOH Quench Volume (cc)	KOH Quench Rate (cc/sec)	NTO Volume (cc)	NTO Velocity (ft/sec)	Combustion Time (microsec)	Gas Release (mol gas/mol NTO)
Complete quenching nozzle No. 4					
165	247	0.96	72		0.005
165	247	0.84			0.005
161	242	1.01	72		0.008
1/8-in I.D., 3/8-in O.D. impingement quench nozzle No. 3					
178	237	0.98	70	94	0.061
178	237	1.02	66	100	0.081
178	237	1.06	68	97	0.095
135	202	0.96	71	93	0.118
134	201	0.92	70	94	0.132

release rates, as in the case of MMH. This behavior again indicates that combustion energy affected quench performance and that the results obtained near 200 microseconds combustion may be generally low.

There was light emission in all the combustion heat release experiments but more for the 200 microseconds tests.

DISCUSSION

RELEASE RATES

The data plotted in Figures 4 through 9 give the following calculated rates of heat and gas release in units of kcal/sec-mol NTO and mol gas/sec-mol NTO, respectively

	N_2H_4	MMH	UDMH
Heat Release Rate			
1st 100 microseconds	4.4×10^4	$> 20 \times 10^4$	14×10^4
2nd 100 microseconds	3.6×10^4		6×10^4
Gas Release Rate			
1st 100 microseconds	400	1200	800
2nd 100 microseconds	750		

Since the gas release mesurements were not corrected for losses to the quench liquid, they are probably slightly low and have less quantitative significance than the heat measurements. However, the gas release rates do tend to corroborate the relative reactivity of the three fuels (based on heat release rates) in the order MMH > UDMH > N_2H_4. In the case of hydrazine, the heat and gas release rates appear to be nearly steady properties of the combustion from 0 to 200 microseconds.

Gas reactions cannot be completely excluded because of the following circumstances. The propellants were discharged at about 50^0 F and atmospheric pressure, the local boiling point of NTO is about 68^0 F, heating the liquid propellant mixtures to the boiling point requires at most 0.9 kcal/mol NTO, and the latent heat for NTO vaporization is about 9 kcal/mol. Hence, in all combustion experiments there was sufficient heat release to vaporize significant amounts of NTO and produce at least gas/liquid reaction over part of the combustion period. In the case of hydrazine, the combustion heat release was never sufficient to completely vaporize the NTO. A major portion of the heat and gas evolved with hydrazine probably resulted from liquid/liquid reaction. In the case of MMH, the release rates almost certainly involve other than liquid/liquid reactions. Heat release with MMH was sufficient for complete NTO vaporization and MMH vaporization as well. With UDMH, the situation was intermediate, and the release rates may again be fairly representative of liquid combustion.

It should be noted that the new experimental technique employed in this program permitted the theoretical residence times to be reduced by about an order of magnitude over those of the technique used in References 3 and 4, and the measured amount of heat released (per mole of propellant) was also decreased by about an order of magnitude. However, even under these conditions, which must approach the limit with respect to minimum reaction times which can be employed for studying liquid-liquid reactions, these hypergolic reactions are so fast that some vapor phase reaction apparently occurs. Even with this limitation, these results will be extremely useful in the modeling and prediction of blowapart.

BLOWAPART

The low boiling point of the propellant mixtures at atmospheric pressure also raises the possibility of blowapart by NTO boiling in the impingement zone. (It is assumed that for immiscible liquids the vapor pressures are additives, Ref. 1). With blowapart, the propellants are prevented from mixing completely, and the resultant heat and gas release per mol NTO discharged is less than with good mixing. A case of perfect blowapart in this experiment would correspond to separate discharge of the propellants into the quench stream, giving only slightly more heat and gas release than for complete quenching. It is possible that the low combustion heat and gas release obtained with hydrazine resulted from blowapart rather than low reactivity; however, this is not likely to be the case.

In a photographic investigation (Ref. 7) of NTO-hydrazine impingement, with about the same temperature conditions, blowapart was not observed with 0.028-inch jets. With larger jets, blowapart was observed to be a cyclical or intermittant process.

Based on the experimental data for NTO-hydrazine, the possibility of blowapart may be discounted since the data show good reproducibility and time continuity. This sort of consistency does not seem compatible with blowapart, which might be expected to yield erratic combustion and poor quantitative reproducibility. In particular, there is the reproducibility in heat release obtained for 200 microseconds combustion, using two different propellant velocities.

With regard to reproducibility, the relatively large spreads in heat and gas release data obtained with UDMH at 100 microseconds combustion could conceivably have resulted from blowapart effects. No experimental cause was established for this poor reproducibility which is therefore ascribed to some source of combustion variability. If blowapart did occur in these UDMH experiments, then the higher heat and gas release values obtained would be even more indicative of the reactivity. Similar speculation in the case of MMH-NTO is prevented by the poor quality of the data, which did not give a good representation of the combustion process. Again, if blowapart is presumed, the MMH-NTO reactivity must be even greater than observed.

REACTIVITY

These experimental data show a large variation in the impingement reactivity of the three fuels with NTO. Reactivity increases sharply in the sequence hydrazine < UDMH < MMH. The predominant combustion energy of MMH is surprising since MMH was generally expected to behave intermediately between the other fuels. There is no basis for questioning this experimental conclusion on the relative NTO impingement reactivity of the three fuels. The fuels were tested under nearly identical conditions and employing the same procedures. In fact, the 100 microsecond quench nozzles used for UDMH and MMH were also tested with hydrazine. It will be of interest if the susceptibilities of these propellant combinations to blowapart are found to correlate with the reactivities determined in this program.

The reactivity scale shown by the fuels with NTO cannot be explained or discussed quantitatively. In broad terms, the NTO impingement reactivity must depend on three main factors: energy of the combustion reaction, propellants mixing, and chemical reactivity. For the three fuels tested, these factors combine to give the observed overall reactivities. With regard to combustion reaction energy, the fuels should be reasonably similar, unless very different intermediate reactions and products are involved. Macroscopic mixing, i.e., liquid/liquid interface generation, rather than molecular miscibility, is probably the primary mixing consideration, since the oxidizer and fuels are not likely to combine appreciably without reaction. In this connection, MMH (24 dynes/cm) and UDMH (34 dynes/cm) have much lower surface tension than hydrazine (67 dynes/cm). Therefore, better intermingling of NTO with MMH or UDMH at impingement is likely leading towards better reactivity than with hydrazine. The chemical or molecular reactivities of the three fuels may be considerably different. The gas phase reaction of hydrazine and nitrogen dioxide proceeds by abstraction of hydrogen from the hydrazine (Ref. 9). If the number of N-H hydrogens is significant, then chemical reactivity would decrease in the order hydrazine, MMH, UDMH. Possibly, the greater overall reactivity of MMH reflects a compromise between mixing efficiency and chemical reactivity. Furthermore, MMH among the three fuels is the only one with a hydrogen bonded to a nitrogen-methyl group. Such a hydrogen atom could be the source of greater chemical reactivity.

VELOCITY EFFECTS

The heat release rate of 4×10^4 kcal/sec-mol NTO for hydrazine falls within the range of 1 to 7×10^4, measured in a prior investigation (Ref. 4), but this agreement appears coincidental in terms of the analysis presented earlier in this report of the previous results. As discussed, the liquid propellants were mixed in that work by fast injection into a confined flow mixer reactor as contrasted to the free-jet impingement mixing used in this case. A range in heat release rates resulted from varying the rate of propellant injection into the mixing chamber (Ref. 4). In the present case, however, a comparable variation in the propellant jet velocity did not affect the heat release rate significantly. This result seems to verify the basic experimental assumptions on combustion time but was not necessarily expected. The kinetic energy of the impinging jets supplies the energy for liquid propellant mixing in the impingement zone. Therefore, the extent of mixing, hence reaction, should be sensitive to the velocity of the impinging streams. Apparently, in hydrazine-NTO free jet impingement complete mixing occurs rapidly with these small jets.

The effect of jet velocity was investigated in one set of tests with hydrazine. If these effects are still absent or reasonably small at higher velocities and with other propellants, there is a possibility of obtaining useful data for combustion times below 100 microseconds.

Such short times were not considered before because construction of quench nozzles with less than 1/8-inch I.D. is difficult and the required jet velocities of 100 to 200 ft/sec would be much greater than are used in rocket engine practice. The possibility of investigating combustion times below 100 microseconds is particularly interesting in the case of MMH and UDMH which showed large heat and gas release rates. One probable experimental difficulty is that increasingly fast propellant discharges imply greater initial energy concentration in the free quench stream. High-energy concentration would tend to impair quench performance, as already happened in some MMH and UDMH experiments. If this is the case, investigation much below 100 microseconds combustion may be possible only with much greater quench velocities than those utilized during the program.

CHEMICAL REACTIONS

These experiments were designed to measure the rates of heat release and gas evolution during the initial contact of hypergolic propellants. The nature and the thermochemistry of the chemical reactions which may have occurred are discussed in Appendix II. It is shown that the amounts of gas evolved for a given amount of heat released are reasonable, but further conclusions regarding reaction stoichiometry cannot be made in the absence of chemical analysis of the reaction products. Also, estimates are made from the heat and gas release data of the quantities of propellant reacted.

CONCLUSIONS

The results obtained in this program lead to the following conclusions:

1. The impinging jet technique allows heat and gas evolution rates of hypergolic reaction to be measured at reaction times of 100 microseconds. This is about an order of magnitude lower than the reaction times that were achieved in earlier studies.
2. The heat and gas evolution rates were very high i.e., on the order of 10^5 kcal/sec.-mol NTO and 1000 mol gas/sec.-mol NTO, respectively.
3. The rates observed were relatively independent of reaction time for a given propellant system. They varied by not more than a factor of two for 100 and 200 microseconds reaction.
4. For a given residence time, a variation in jet velocity from 80 to 40 ft/sec did not affect the heat evolution rate.
5. The heat and gas evolution rates are definitely dependent on the propellant system. This was found to be the case even though the oxidizers, NTO, was the same in the three systems studied, and the fuels belonged to the same family, i.e., hydrazine, MMH, and UDMH. The MMH/NTO system exhibited the highest heat and gas evolution rates.

RECOMMENDATIONS

It is recommended that based on the data obtained in this investigation the apparatus and technique described be utilized to extend further our understanding of liquid/liquid propellant interactions.

Some of the areas recommended for further study are

1. Effects of pressure and temperature
2. Effect of surface tension
3. Reaction times shorter than 100 microseconds
4. Clarification of reasons for the observed differences in heat and gas evolution rates of the three systems studied.

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APPENDIX I

QUENCH REACTIONS

It was determined during the initial quenching only experiments in the impingement apparatus that the heat of quenching for a mixture of hydrazine and NTO was quite variable, depending upon the type and rate of mixing employed. Quench heats ranged from about 30 to 60 kcal per mol of NTO for different mixing conditions (in the impingement experiments the N_2H_4/NTO mol ratio was always about 2.4 so that the quench heats are reported "per mol of NTO" but include the heat released from the reaction of the 2.4 mol of N_2H_4 that is also "quenched"). A literature search and theoretical analysis were conducted to determine if the quench reaction could be made more reproducible. In addition, a number of quench conditions were investigated in a laboratory calorimeter.

THEORETICAL

Neutral Water Quench

The ideal quench reaction for NTO and hydrazine in neutral water is that in which the NTO reacts with water to form nitrous and nitric acid and these acids are neutralized by the excess hydrazine to form, respectively, hydrazinium nitrite and hydrazinium nitrate. The thermochemistry of the individual reactions involved are as follows (all heats were calculated from data given in the NBS circular No. 500 and the JANNAF Thermochemical Tables):

(1) $2.4\ N_2H_4(l) \rightarrow 2.4\ N_2H_4(aq)$ $\Delta H = -9.4$ kcal

(2) $N_2O_4(l) + H_2O \rightarrow H^+ + NO_3^- + HNO_2$ $\Delta H = -4.8$ kcal

(3) $N_2H_4(aq) + H^+ \rightarrow N_2H_5^+$ $\Delta H = -9.9$ kcal

(4) $\underline{N_2H_4(aq) + HNO_2 \rightarrow N_2H_5^+ + NO_2^-}$ $\underline{\Delta H = -6.9 \text{ kcal}}$

(5) $N_2O_4(l) + 2N_2H_4(aq) + H_2O \rightarrow 2N_2H_5^+ + NO_2^- + NO_3^-$ $\Delta H = -21.6$ kcal

adding equations 1 and 5 gives the overall theoretical quench reaction:

$$(6)\ N_2O_4(l) + 2.4\ N_2H_4(l) + H_2O \rightarrow$$
$$0.4\ N_2H_4(aq) + 2N_2H_5^+ + NO_2^- + NO_3^- \qquad \Delta H = -31.0 \text{ kcal}$$

It can be seen that if only the theoretical quench reactions occur, considerable heat will still be released from the quenching of unreacted propellant. The theoretical quench reaction does not, however, involve the evolution of any gaseous products.

A review of the literature indicated that the most likely side reactions under the water quench conditions are the decomposition of nitrous acid (Ref. I-1 through I-7).

$$(7)\ HNO_2 \rightarrow 1/3\ H^+ + 1/3\ NO_3^- + 2/3\ NO + 1/3\ H_2O \qquad \Delta H = +3.5 \text{ kcal}$$

or the reaction of nitrous acid with hydrazine (Ref. I-8 through I-17) according to either of the following overall stoichiometries:

$$(8)\ HNO_2 + N_2H_4(aq) \rightarrow NH_3 + H_2O + N_2O \rightarrow NH_4OH + N_2O \qquad \Delta H = -47.7 \text{ kcal}$$
$$(9)\ HNO_2 + 1/2\ N_2H_4(aq) \rightarrow 1/2\ N_2 + 1/2\ N_2O + 3/2\ H_2O \qquad \Delta H = -68.4 \text{ kcal}$$

If all of the nitrous acid decomposed (Reaction 7 in place of Reaction 4) and the nitric acid formed in Reaction 7 is also neutralized by Reaction 3, the overall quench reaction would become

$$(10)\ N_2O_4(l) + 2.4\ N_2H_4(l) + 2/3\ H_2O \rightarrow$$
$$1.07\ N_2H_4(aq) + 4/3\ N_2H_5^+ + 4/3\ NO_3^- + 2/3\ NO \qquad \Delta H = -23.9 \text{ kcal}$$

If all the nitrous acid reacted by Reaction 8,

$$(11)\ N_2O_4(l) + 2.4\ N_2H_4(l) + H_2O \rightarrow$$
$$0.4\ N_2H_4(aq) + N_2H_5^+ + NO_3^- + NH_4OH(aq) + N_2O \qquad \Delta H = -71.8 \text{ kcal}$$

If all of the nitrous acid reacted by Reaction 9,

$$(12)\ N_2O_4(l) + 2.4\ N_2H_4(l) \rightarrow \qquad \Delta H = -92.5 \text{ kcal}$$
$$0.9\ N_2H_4(aq) + N_2H_5^+ + NO_3^- + 1/2\ N_2 + 1/2\ N_2O + 1/2\ H_2O$$

It can be seen, therefore, that the most likely side reactions when using water as the quench liquid (Reactions 7, 8, and 9) give quench heats which range from 24 to 92 kcal per mol NTO and quench gas evolutions of 2/3 to 1 mol of gas per mol NTO.

If the four possible quench reaction paths proposed above occur to various extents depending upon the mixing conditions, this would account for the wide range of quench heat values that were obtained when water was used as the quench liquid. The literature references cited above indicate that the rates of Reactions 7, 8, and 9 are strongly dependent on pH, reactant concentrations, and temperature, as well as on certain physical processes, such as the rate of removal of gaseous reaction products. It is not too surprising, therefore, that a variable quench stoichiometry was obtained since during the mixing of the propellants with the water the local pH, concentrations, and temperatures may vary widely. The variation in quench heat indicates that at least one of these side reactions can compete with Reaction 4 under some conditions.

Basic Solution Quench

The information obtained from the literature indicates that the rates of Reactions 7, 8, and 9 are all strongly pH-dependent (acid catalyzed). This suggested that a more reproducible quench stoichiometry might be obtained if a very basic quench solution were used. Experiments conducted in a laboratory calorimeter (discussed in the next section) tended to confirm this hypothesis. Quenching only experiments conducted in the impingement apparatus with a 3 molar KOH quench solution gave very reproducible quench heats under a variety of flow conditions. The quench heats obtained with the basic quench solution were always very near the theoretical value for complete neutralization (derived below). This basic quench solution was employed in all of the impingement experiments reported in the text of this report. KOH was chosen because its high solubility in water permits very basic quench solutions to be prepared. In addition to the inhibition of the side reactions by the high pH of the quench solution, the high OH^- concentration should permit the HNO_2 to be neutralized much more rapidly, again tending to favor neutralization of HNO_2 over its other possible reactions. The excess hydrazine does not give a sufficiently basic solution (when neutral water is employed) because hydrazine behaves as a weak base in water with the following basicity constant:

(13) $(N_2H_5^+)(OH^-)/(N_2H_4) = 8 \times 10^{-7}$ mol/liter

In basic solution, the hydrazine should not participate in the quench reaction, and the overall theoretical quench reaction would then be composed of the following steps:

(1) $2.4\ N_2H_4(l) \rightarrow 2.4\ N_2H_4(aq)$ $\Delta H = -9.4$ kcal

(2) $N_2O_4(l) + H_2O \rightarrow H^+ + NO_3^- + HNO_2$ $\Delta H = -4.8$ kcal

(14) $OH^- + H^+ \rightarrow H_2O$ $\Delta H = -13.3$ kcal

(15) $OH^- + HNO_2 \rightarrow H_2O + NO_2^-$ $\Delta H = -10.3$ kcal

(16) $N_2O_4(l) + 2.4\ N_2H_4(l) + 2\ OH^- \rightarrow$
$2.4\ N_2H_4(aq) + NO_2^- + NO_3^- + H_2O$ $\Delta H = -37.8$ kcal

It may be seen from Fig. 2 that the quench heats obtained in KOH-solution quenching only experiments with NTO and hydrazine are near this theoretical value, and the gas evolution from the quench reaction is small, indicating that the undesired side reactions only occurred to the extent of about one percent.

Quench Solution Containing the Salt of a Weak Acid

The use of a salt of a weak acid instead of KOH has the advantages of easier handling of the solution (less caustic at high concentrations) and lower theoretical heats of quenching. It turns out, however, that salts that have very low theoretical heats of quenching generally cannot compete effectively with hydrazine for the protons formed in the reaction of NTO with water. For example, a solution of Na_2HPO_4 has a theoretical quench heat of only -6 kcal per mol of NTO, but the neutralization product, $H_2PO_4^-$, has such a large dissociation constant that it does not form in preference to the $N_2H_5^+$ ion (Reactions 3 and 4), the formation of which gives the theoretical quench heat of Reaction 6 (-31.0 kcal). However, in the case of a solution of Na_3PO_4, the theoretical quench heat is -26.5 kcal per mol NTO (see next paragraph) and the equilibria involved favor the formation of the HPO_4^{-2} ion over the $N_2H_5^+$ ion. The use of a weak salt quench solution was investigated theoretically and in a (small) experimental effort to have it ready as a back up for use in the impingement apparatus in the event strong caustic solutions were found to be incompatible.

When K_3PO_4 is added to water, the following reaction occurs to a small extent:

(17) $PO_4^{-3} + H_2O \rightleftharpoons HPO_4^{-2} + OH^-$

In a 3 M phosphate quench solution, for example, the ionic concentrations are calculated to be: $(PO_4^{-3}) = 2.76$ M, $(HPO_4^{-2}) = (OH^-) = 0.234$ M. It can be seen that for the phosphate ion to neutralize acid according to the reaction:

(18) $PO_4^{-3} + H^+ \longrightarrow HPO_4^{-2}$

some of the acid must also be neutralized by the OH^- ion so that Reaction 17 can remain at equilibrium. It turns out that when 0.045 mol per liter of NTO is neutralized by a 3 M KOH solution, 57.7% of the acid will be neutralized by Reaction 18 and 42.3% by reaction with OH^- to form H_2O. The heat of neutralization of NTO by phosphate ion is 8.8 kcal per mol of liquid NTO added. The similarly defined heat of neutralization by OH^- is 28.4 kcal per mol of NTO (the sum of Reactions 2, 14 and 15). Thus, the theoretical heat of neutralization of NTO in 3 M phosphate solution is 17.1 kcal per mol of NTO. When the heat of solution of 2.4 mol of hydrazine (9.4 kcal, Reaction 1) is added to this, the expected heat of quenching of the NTO/hydrazine mixture becomes 26.5 kcal per mol of NTO.

Quench Reactions with MMH and UDMH

It can be seen from Reactions 1, 2, 14, and 15 that 75 percent (28.4 kcal) of the heat of quenching of NTO and hydrazine in a KOH quench solution comes from the reaction of NTO with the quench solution. The other 25 percent (9.4 kcal) is the heat of solution of the 2.4 mol of hydrazine that remains unreacted. For the quenching of mixtures of MMH and UDMH with NTO in a basic quench solution, the heat of quenching from the NTO should remain the same, with the remainder of the heat again being the heat of solution of the fuel. It should be noted, that in the impingement and quench experiments with MMH and UDMH the fuel-to-oxidizer mol ratios were only 1.64 and 1.17, respectively, compared to 2.40 for the hydrazine experiments, thereby reducing the contribution of the heat of solution of the fuel to the overall heat. Since the heats of solution of MMH and UDMH in water have not been reported, it was assumed that they were the same as for hydrazine (3.9 kcal per mole of hydrazine). The theoretical basic quench heats were thus estimated as 34.8 kcal per mol NTO for the NTO/MMH mixture and 32.9 kcal per mol NTO for the NTO/UDMH mixture. These theoretical values were again within one kcal of the measured quench only heat values shown in Figures 4 and 6 for these fuels.

QUENCH TESTS IN LABORATORY CALORIMETER

Because of the criticality of a reproducible quench reaction, supporting experiments were conducted in a dewar-type laboratory calorimeter. In each experiment, the dewar initially contained 500 ml of water or an aqueous solution. Hydrazine or NTO was rapidly introduced into the solution, and after the temperature rise from that process had been established (about 10 minutes), the other propellant was introduced and the second temperature rise recorded. The propellant quantities were such that the NTO concentration was about 0.05 M (measured accurately by weighing the NTO ampoule before each experiment), and the hydrazine concentration about 0.12 M (measured only with a syringe because the hydrazine is always in excess). The molar ratio of hydrazine to NTO was 2.4 in each experiment to correspond to the relative quantities employed in the impingement experiments. It can be seen that two conditions could be investigated--the reaction of concentrated hydrazine with dilute NTO, and that of concentrated NTO with dilute hydrazine. The solution was stirred with a magnetic stirrer and the calorimeter was purged with N_2. No gas evolution measurements could be made with this apparatus.

Quenching in Neutral Water

In the absence of the decomposition of HNO_2, or a direct reaction between NTO and hydrazine (other than neutralization), the neutralization of NTO by excess hydrazine should proceed according to Reaction 6 with a heat of -31.0 kcal per mol of NTO. In the initial experiment with water in the calorimeter, the hydrazine was introduced first, giving a heat release of 9.2 kcal/mol-oxidizer (in agreement with Reaction 1). However, the introduction of the NTO gave 43.1 kcal/mol which is twice the theoretical heat for Reaction 5. The total heat of neutralization in this experiment was 52.3 kcal/mol which is 21.3 higher than the theoretical value of 31.0 for Reaction 6.

In a second experiment with water, the NTO was introduced first, giving 4.0 kcal/mol (vs. a theoretical value of 4.8 for Reaction 2) and then the hydrazine, giving 35.6 kcal/mol-oxidizer. The total heat of quenching in this experiment was 39.6 kcal/mol, which exceeds the theoretical value by 8.6 kcal/mol. These two water experiments are listed first in Table I-1.

The excess heat of quenching in water, above that predicted for Reaction 6, must result from direct reactions between hydrazine and NTO or HNO_2 such as Reactions 8 and 9. These results and those obtained

TABLE I-1. SUMMARY OF N_2H_4/NTO QUENCH EXPERIMENTS IN LABORATORY CALORIMETER

Conditions	KOH Concentration, Molar	Observed Heat, kcal/mole-NTO	Theoretical Heat, kcal/mole-NTO	Excess Heat*
NTO Added First	None	39.6	31.0	8.6
N_2H_4 Added First	None	52.3	31.0	21.3
N_2H_4 Added First, only heat of NTO Addition Measured	0.01	48.7, 51.5	28.4**	20.3, 23.1
"	0.1	45.9	28.4**	17
"	0.9	34.5	28.4**	6.0
"	1.0	38.0	28.4**	9.6
"	1.9	33.6	28.4**	5.2
NTO Added to KOH Solution, no N_2H_4 Present	0.9	27.5, 29.5	28.4**	0 ± 1.0

* Attributed to undesirable side reactions other than simple neutralization.

**Theoretical heat of reaction between NTO and KOH quench solution because hydrazine should not react (sum of Reactions 2, 14 and 15) in quenching experiments in the impingement apparatus indicate that neutral water is not a satisfactory quench fluid because the heat of quenching is variable, depending on how the propellants are introduced into the fluid.

Quenching in KOH Solution

In basic solution, the hydrazine should not participate in the quench reaction. The overall theoretical reaction is then given by equation 16. A series of experiments were conducted to determine the concentration of KOH required to reduce or eliminate the detrimental side reactions. In these experiments the hydrazine and KOH were added to the water before placing it in the calorimeter. Thus the measured heat is only that due to NTO introduction. These results are listed in Table I-1.

It may be seen from the last line in Table I-1 that in the absence of hydrazine the theoretical heat of quenching in KOH is obtained. With 0.01 M KOH the heat of the side reactions was about the same as with water, i.e., around 21 kcal/mol of excess heat, even though the OH^- concentration in 0.01 M KOH is higher by a factor of 100 than in 0.12 M N_2H_4. The amount of excess heat evolved decreased with increasing KOH concentration, reaching a value of 5 kcal/mol for the one experiment in 1.9 M KOH. These results indicated that high concentrations of strong base in the quench water should be very beneficial, but some side reaction might still occur. The 3 M KOH solution used in the impingement apparatus was not tested in the laboratory colorimeter but the results obtained in the quenching only experiments indicate that 3 M KOH virtually prevents any side reactions from occurring.

Quenching in Na_3PO_4 Solution

When an NTO ampoule was broken in a 0.26 M Na_3PO_4 solution in the laboratory calorimeter the heat release was 18.1 kcal/mol. The subsequent addition of hydrazine to this solution released an additional 9.4 kcal per mole of NTO (Reaction 1) giving a total heat release of 27.5 kcal. The theoretical heat under these conditions (which is slightly smaller than in the theoretical example for 3 M K_3PO_4 because of the lower concentration of phosphate) is 16.2 + 9.4 = 25.6 kcal.

Reversing the order and adding the hydrazine first to the phosphate solution gave heat releases of 8.3 + 17.1 = 25.4 kcal per mole of NTO. These are close to the theoretical heats which are again 9.4 + 16.2 = 25.6 kcal. It should be noted that when a similar experiment was run with water as the quench liquid, a heat was obtained which was greater than the theoretical heat by 21.3 kcal (Table I-1). It thus appears that the phosphate ion neutralizes the NTO before it can react with the hydrazine. This result is somewhat surprising because KOH was not as effective at this low a concentration. Also, Na_3PO_4 at this concentration was found not to be satisfactory in a few quench experiments conducted in the actual impingement apparatus. It appeared that K_3PO_4 (which is much more soluble than Na_3PO_4) at high concentration would have been a promising backup for the KOH quench, should it have run into difficulty.

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APPENDIX II

DISCUSSION OF COMBUSTION REACTIONS

The nature and thermochemistry of the combustion reactions that occur between the oxidizer and fuel and give rise to the measured heat and gas release rates (in addition to those of the quench reactions) are discussed in this appendix.

HYDRAZINE/NTO REACTIONS

The complete combustion (reaction) of NTO and hydrazine would give the following stoichiometry:

(19) $N_2O_4(l) + 2\ N_2H_4(l) \longrightarrow 3\ N_2 + 4\ H_2O$

If the experimental conditions are such that the water is condensed (as in the case for the present study), the heat of Reaction (19) is -293 kcal per mol NTO.

There is every likelihood, however, that the reaction of NTO and hydrazine in the liquid phase will not go to completion and will lead to the formation of appreciable quantities of products such as hydrazinium nitrate, ammonia, and possibly hydrazinium nitrite. It is apparent, therefore, that only speculations can be made as to the exact nature of the chemical reactions responsible for the heat and gas released during the impingement experiments. Perlee et al (Ref. II-1) and Weiss (Ref. II-2) have each proposed stoichiometries for the formation of hydrazinium nitrate from NTO and hydrazine. These are, respectively:

(20) $N_2O_4 + 3/2\ N_2H_4 \longrightarrow 1/2\ H_2O + 1/2\ N_2O + 1/2\ N_2 + N_2H_5NO_3$

(21) $N_2O_4 + 2\ N_2H_4 \longrightarrow N_2O + NH_3 + N_2H_5NO_3$

In the presence of an aqueous quench liquid, these two reactions would give the following overall reactions:

$$(22) \quad N_2O_4(l) + 3/2\ N_2H_4(l) \longrightarrow 1/2\ H_2O\ (l) + 1/2\ N_2O + 1/2\ N_2 + N_2H_5^+ + NO_3^- \qquad \Delta H = -89 \text{ kcal}$$

$$(23) \quad N_2O_4(l) + 2\ N_2H_4(l) + H_2O(l) \longrightarrow N_2O + NH_4OH(aq) + N_2H_5^+ + NO_3^- \qquad \Delta H = -69 \text{ kcal}$$

Reactions leading to the formation of hydrazinium nitrite are also possible but it is expected that most of the nitrite would be rapidly oxidized by NTO.

Limiting the following discussion to the three combustion reactions proposed in the previous paragraph, the heat of combustion in the impingement experiments could range from 70 to 293 kcal per mol of NTO reacted. From this estimated range for the heat of combustion, the amount of propellant reacted during the impingement experiments can be estimated. The heat released per 100 microseconds in the NTO/hydrazine experiments was about 4 kcal per mol of NTO passed through the reactor (Figure 2). Thus the percent NTO that reacted per 100 microseconds can be estimated to be in the range of 1.3 to 5.7 percent. From equations 19, 20, and 21, the moles of hydrazine reacted per mole of NTO should be between 1.5 and 2. Because the hydrazine/NTO mol ratio was 2.4 in these experiments the estimated percent hydrazine reacted per 100 microseconds ranges from 0.8 to 4.7 percent.

From the above estimates of the amounts of propellant reacted, the decrease in heat of quenching with reaction time can be estimated (as discussed in the text, this decrease results from less unreacted propellant remaining to be quenched). The minimum decrease per 100 microseconds is calculated to be 0.4 kcal per mol NTO (0.013 x 28.4 + 0.008 x 9.4) and the maximum 2.0 kcal per mol NTO (0.057 x 28.4 + 0.047 x 9.4). Since the measured heat release per 100 microseconds was about 4 kcal per mol NTO, <u>the reported heat release rates for hydrazine/NTO need to be increased by 10 to 50 percent depending upon the actual value of the heat of the combustion reaction</u>.

A comparison of the measured heat and gas release rates for NTO/hydrazine can be made in terms of the reaction stoichiometries hypothesized above. Reactions 19, 22 and 23 indicate, respectively, the following ratios of heat release to gas release: 98, 89 and 70 kcal per mol of gas. The results from the impingement experiments yield a ratio of 110 kcal per mol of gas during the first 100 microseconds ($4.4 \times 10^4 \div 400$) and 48.0 for the second 100 microseconds. The change in this calculated ratio with reaction time results from the apparent break in the gas evolution curve. This break in the gas evolution curve suggests that the reaction stoichiometry changes with reaction time. It may be seen from Figure 3, however, that a linear curve indicating a constant gas evolution rate would almost be within the experimental error. An assumed constant rate of gas evolution over a 200 microsecond reaction time yields a ratio of heat release to gas release of about 75 kcal per mol gas. Since the reported heat release rates are low by 10 to 50 percent, the gas release rates are seen to be in the range predicted by the postulated combustion reactions.

REACTIONS OF MMH AND UDMH WITH NTO

Considerations similar to those for N_2H_4/NTO can be made for the MMH/NTO reactions although no stoichiometries have been proposed for the incomplete reactions in which MMH nitrate would form. Mayer et al (Ref. II-3) have proposed the following reactions for the complete combustion of MMH:

$$(24)\quad \text{MMH} + N_2O_4 \longrightarrow 3\,H_2O + 2\,N_2 + CO$$

$$(25)\quad \text{MMH} + 1.25\,N_2O_4 \longrightarrow 3\,H_2O + 2.25\,N_2 + CO_2$$

These reactions have heats of reaction (under the test conditions) of 240 and 245 kcal per mol NTO, respectively. The heat release to gas release ratios are 80 and 94 kcal per mol of gas for these two cases.

It can be shown that if the complete combustion stoichiometries occur, the observed heat release rate for MMH/NTO (20 x 10^4 kcal/mol NTO-sec) represents 8 percent of the NTO reacted per 100 milliseconds. The formation of MMH nitrate (giving a lower heat of reaction) would require that even more MMH react to give the observed heat release rates. The correction of the heat release rate for the change in the amount of propellant quenched turns out to be only about 13 percent if the heat of combustion is 240 kcal but will be higher if incomplete combustion products form.

The ratio of the observed heat to gas release rates for MMH/NTO is 166 kcal per mol gas (20 x 10^4 ÷ 1200). This ratio is about twice that expected if the products are N_2, H_2O and CO_2 or CO, indicating that other reaction products are probably involved.

Similar calculations can be made for UDMH/NTO reactions but, considering the uncertainties in the reaction stoichiometries, this was not done.

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APPENDIX III

MISCIBILITY OF NTO AND HYDRAZINE

The possible miscibility of hydrazine and nitrogen tetroxide was evaluated theoretically. A limited investigation indicates that the propellants should be considered mutually insoluble in modeling their mixing. Solution between these two propellants would require strong specific association between their molecules, mostly because the hydrazine is itself associated by hydrogen bonding. The most likely solution association is also hydrogen bonding between the two species. However, the strength of this association is probably insufficient, and, more significantly, hydrogen bonding and transfer probably establish the combustion reaction. Therefore, appreciable solution of the unreacted propellants is unlikely.

The thermodynamic prediction of equilibrium solubility proceeds by estimating the molal free-energy change on mixing according to a relation of the type (Ref. III-1, III-2):

$$F = RT\ (X_1\ \ln X_1 + X_2\ \ln X_2) + \frac{X_1V_1X_2V_2}{X_1V_1 + X_2V_2}\ (C_{11} + C_{22} - 2C_{12})$$

where subscripts 1, 2 refer to the two components nitrogen tetroxide and hydrazine, X is mole fraction, V is molal volume. The quantities C are cohesive energy densities for each pure liquid (C_{11}, C_{22}) and for mixed interaction (C_{12}), one species in an environment of the other. This and similar approximations for the free-energy change on mixing are not generally accurate for solubility calculations. However, the equation does indicate the basic features of solubility and is useful for preliminary considerations. The first terms of the free-energy expression correspond to the ideal entropy change on mixing. This contribution is negative and such that some solubility is always expected. The extent of solubility then depends on the relative magnitude of the internal energy change from mixing. If the mixed energy (C_{12}) is comparable to or greater than the mean of the unmixed energies (C_{11}, C_{12}) solution is possible over a broad range in composition. On the other hand, if mixing is energetically unfavorable (relatively small C_{12}), then solubility will be limited and may be negligible.

The cohesive energy densities of the pure substances may be estimated from their heats of vaporization. At about 300 K nitrogen tetroxide has $C_{11} = 100$ cal/cc and hydrazine $C_{22} = 320$ cal/cc approximately; the nitrogen tetroxide estimate has been corrected for the partial decomposition to nitrogen dioxide on vaporization. The molal valumes are $V_1 = 64$ cc and $V_2 = 32$ cc. For complete solubility, the mixed energy C_{12} would have to be at least 190 cal/cc, and even for slight solubility, say less than one mole percent, at least 170 cal/cc. The simplest estimate of mixed energy for non-electrolyte solutions involving largely van der Waals intermolecular forces is the geometric mean of the unmixed energies, in this case about 180 cal/cc. According to these considerations, hydrazine and nitrogen tetroxide would appear to have some mutual solubility. However, these propellants do not constitute an ordinary solution system. Nitrogen tetroxide is a reasonably normal unassociated liquid, but hydrazine, as indicated by its relatively large dielectric constant, surface tension, boiling point, etc., is strongly associated, presumably by hydrogen bonding (NH-N). The cohesive energy due to hydrogen bonding in hydrazine has not been reliably estimated, but it is probably well over half the total, by comparison with normal liquids. Of itself, this strong specific association in the one liquid simply increases the energy required for mixing and further reduces the solubility. The present case has the added complication that the specific association is transferrable to the solution in that hydrazine could also form hydrogen bonds (NH-O) to nitrogen tetroxide.

Hence, a formal solubility estimate requires assigning good values to both the hydrogen bonding in hydrazine and in the mixture. Lacking this knowledge, the question of solubility is left open. For example, if the hydrogen bonding in hydrazine contributes between half and all the total cohesive energy, and this bonding is completely transferred to the mixture, the system shows total solubility (C_{12} = 290 - 350 cal/cc); if half the hydrogen bonding energy is transferred, there could be varying degrees of solubility (C_{12} = 160 - 210 cal/cc); if no hydrogen bonding is assigned to the mixture, solubility is negligible (C_{12} = 0 - 130 cal/cc). A general classification of hydrogen bond energies (Ref. III-3) shows NH-O bonding to be less than half as strong as NH-N. On that basis alone, the propellants tend to low mutual solubility even with mixed hydrogen bonding.

Moreover, mixed hydrogen bonding is not likely to promote solubility without reaction. Solubility in this system means molecular mixing in spite of the potential for reaction, so that the possible concentration of dissolved species depends also on the mechanism and kinetics of the combustion reaction. The gas-phase reaction between hydrazine and nitrogen dioxide is partly controlled by an initiating step of hydrogen abstraction from the hydrazine (Ref. III-4). Hydrogen bonding in solution would establish this reaction step and, although calculation has not attempted, extensive bonding in the mixture without reaction seems unlikely. Excluding this possible association in solution, the propellants have negligible mutual solubility.

The above considerations refer to the mutual solubility at thermodynamic equilibrium. In an actual mixing process, this limiting equilibrium solubility would be ultimately reached by interdiffusion of the unreacted propellants. Therefore, the possible significance of any mutual solubility in the mixing process depends additionally on the relative efficiency of diffusion transport. On the basis of linear semi-infinite diffusion, the average penetration depth of the equilibrium concentration from one liquid into the other in a time t is approximately the square root of Dt, where D is the diffusion coefficient, typically 10^{-5} cm^2/sec for liquids. The characteristic times for reaction, as well as the residence times available for mixing in a free-jet impingement zone, are on the order of 100 microseconds (Ref. III-5, III-6). Hence, solution mixing involves liquid layers on the order of 10^{-4} cm thick. Such thin layers may be considered as a surface contact between insoluble liquids, unless the bulk phases being mixed are subdivided down to comparable dimensions, e.g., drop diameters of 10^{-3} cm and less. These dimensions are reasonably small in comparison to the impingement zone, so that the mixing is probably dominated by contact between much larger bulk fragments. In addition, the occurrence of the very small drops would generally imply a gradual process of subdivision and hence an entire range of larger drop sizes. Therefore, the possible solution mixing, if any, could be effectively regarded as a surface effect.

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APPENDIX IV

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