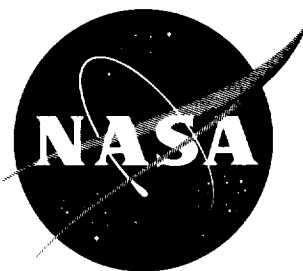NASA TN D-469

TECHNICAL NOTE

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DIMETHYLHYDRAZINE - NITRIC ACID
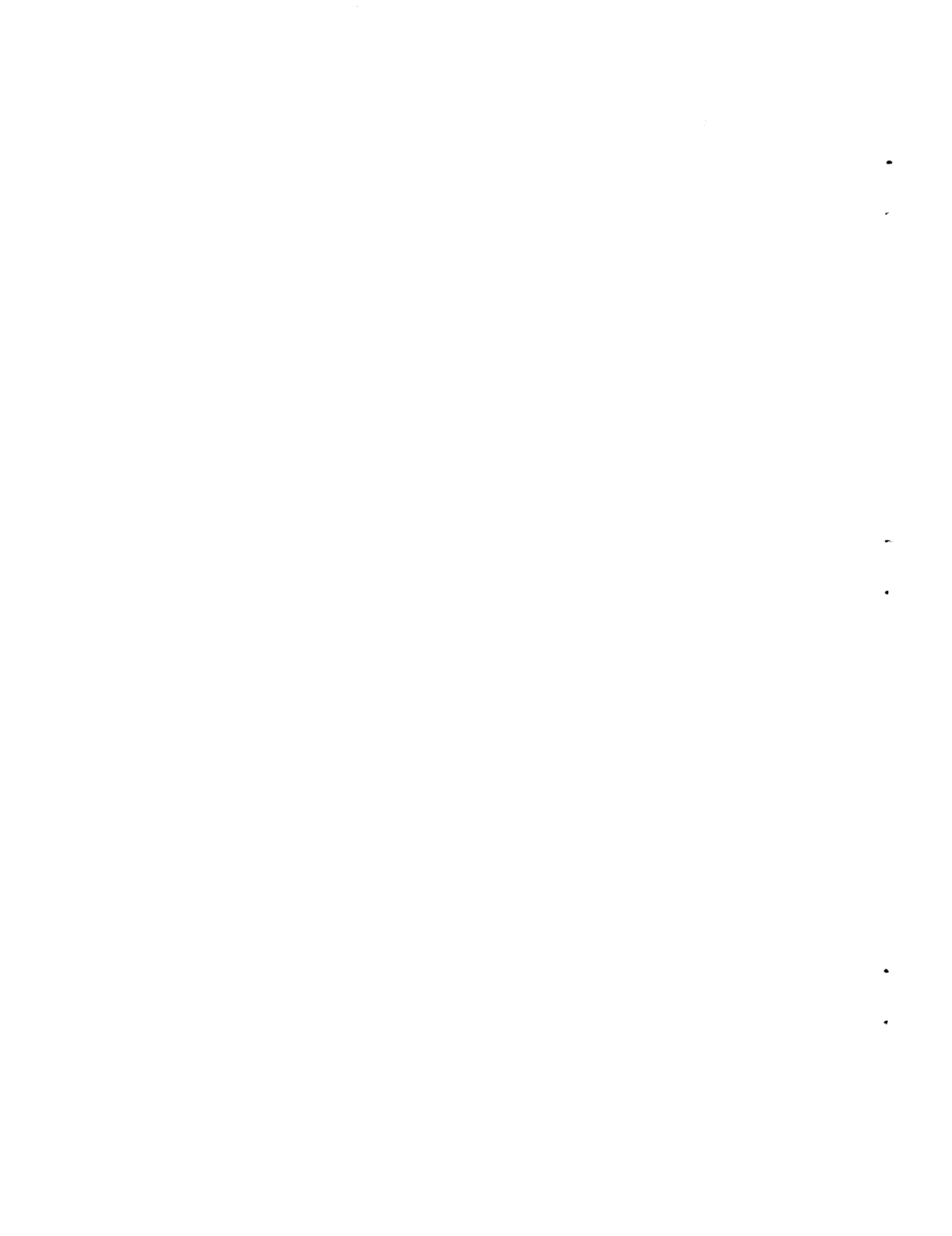
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TECHNICAL NOTE D-469

LIQUID-PHASE HEAT-RELEASE RATES OF THE SYSTEMS HYDRAZINE - NITRIC

ACID AND UNSYMMETRICAL DIMETHYLHYDRAZINE - NITRIC ACID

By Dezso Somogyi and Charles E. Feiler

SUMMARY

The initial rates of heat release produced by the reactions of hydrazine and unsymmetrical dimethylhydrazine with nitric acid were determined in a bomb calorimeter under conditions of forced mixing. Fuel-oxidant weight ratio and injection velocity were varied. The rate of heat release apparently depended on the interfacial area between the propellants. Above a narrow range of injection veloc- ities representing a critical amount of interfacial area, the rates reached a maximum and were almost constant with injection velocity. The maximum rate for hydrazine was about 70 percent greater than that for unsymmetrical dimethylhydrazine. The total heat released did not vary with mixture ratio over the range studied.

INTRODUCTION

Recent findings in rocket combustion studies have led to a com- bustion model based on vaporization of one of the propellants as the rate-limiting step for systems such as hydrocarbon-oxygen (refs. 1 to 3) and to a distillation theory for systems such as hydrocarbon - nitric acid (ref. 4). Neither of these models has considered the effects of liquid-phase reaction and associated heat release on com- bustion. For systems in which propellants are mixed during injection, the extent and rate of liquid-phase heat release may be important factors in combustion.

The objective of this study, therefore, was to obtain data on the amount and rate of heat release produced by liquid-phase reaction of typical self-igniting propellant systems. The propellant combina- tions studied were hydrazine (N_2H_4) - nitric acid (HNO_3) and unsym- metrical dimethylhydrazine (UDMH) - nitric acid.

The apparatus consisted of a constant-volume calorimeter, in which the calorimetric fluid also served to quench the reaction, and a rapid-mixing injection device. Propellants were injected through

a mixing cup of constant area and variable length. On emerging from the cup the reaction was quenched and the pressure and temperature rise were measured. From these data a heat-release rate was obtained as a function of the injection velocity. An effort was also made to correlate pressure and heat-release data in terms of the contribution from each of several reactions that can occur.

APPARATUS AND PROCEDURE

The apparatus (fig. 1) was essentially the same as the one used in the investigation of reference 5 except for some modifications to adapt it to the present study. It consisted of a Plexiglas-lined chamber, a premixing injector, cylinders containing propellant, pistons, and a quick-opening valve. The chamber volume was divided into two parts: the upper part, which was about two-thirds of the total volume and contained the quenching medium, and the lower part, which acted as a surge tank.

Injection was accomplished by triggering the quick-opening valve, which discharged high-pressure nitrogen gas against the driver piston to force the propellants to break through the Teflon gasket and be mixed in the cup. When the mixture emerged from the cup, the reaction was stopped before going to completion by the quenching fluid. The temperature rise of the quenching fluid was measured by a resistance thermometer and recorded by a potentiometer. The temperature was extrapolated back to zero time to compensate for the heat lost during the time of temperature rise. The heat release was calculated from the extrapolated temperature (shown in fig. 2), the mass, and the specific heat of the quenching fluid. The pressure rise due to the reaction was measured by a Bourdon tube pressure gage.

The apparatus was checked for accuracy with solutions of hydrogen chloride and sodium hydroxide. The difference between the experimental heat release and the theoretical value was less than one-half of 1 percent.

The mixing efficiency of the injector was determined with aqueous-dye-solution injection by the method described in reference 6 and was found to be 94 percent. Water injection was used to determine the flow velocity through the mixing cup. For this determination the mixing cup was wired as shown in figure 3. Water shorted out the wires as it flowed through the cup, and the resulting electrical signals were recorded by an oscilloscope. The flow velocity was calculated from the distance between wires and the time between signals. Velocity as a function of driver gas pressure is also shown in figure 3. Similar results for this type of apparatus were found in reference 7, where it is stated that the injection rate of water was constant throughout the injection period.

Mixing-cup length varied from 0.31 to 1.06 inches, while the driver gas pressures were 200, 500, 800, 1000, 1500, and 2000 pounds per square inch gage (which correspond to injection velocities from 60 to 190 ft/sec). Throughout this experiment the total volume of propellants was held constant at 2 cubic centimeters. The volume ratios of acid to fuel studied and the corresponding weight and mole ratios are summarized in the following table:

	$\dfrac{HNO_3}{N_2H_4}$		$\dfrac{HNO_3}{UDMH}$		
Volume ratio	1.0	1.50	0.67	1.00	1.50
Weight ratio	1.5	2.25	1.28	1.91	2.87
Mole ratio	0.76	1.14	1.22	1.82	2.73

RESULTS AND DISCUSSION

Total Heat Release and Equilibrium Pressures

The experimental total heat release in the reaction of hydrazine and UDMH with nitric acid is shown in figure 4 as a function of mixing-cup length. A linear increase in heat release with cup length was observed for both fuels (fig. 4(a)). The quantity of heat reached a maximum at a driver pressure of about 1000 pounds per square inch gage and at this pressure was about 50 percent larger for hydrazine than for UDMH. The total heat released was independent of mixture ratio over the range studied (fig. 4(b)). At zero cup length a finite constant heat release was obtained experimentally. This heat was probably composed of heat of solution of unreacted or excess fuel or acid in water and of heat of neutralization of acid with fuel.

The equilibrium pressures produced by the reactions are shown in figure 5 as a function of mixing-cup length. The pressure rise and the heat release were from 10 to 30 percent of the theoretical values for complete combustion, which indicated that appreciable quantities of gaseous products were formed.

Heat-Release Rates

Evolution of gas in the mixing cup could result in an accelerating flow whose rate would have to be known in order to obtain heat-release rates. It is possible to obtain an initial heat-release rate by assuming that the velocity at the entrance to the mixing cup was equal to that measured in cold-flow calibrations. Thus, the heat-release rate at zero cup length is given by

$$\left(\frac{dQ_{exp}}{dt}\right)_{L\to 0} = \left(\frac{dQ_{exp}}{dL}\right)_{L\to 0}\left(\frac{dL}{dt}\right)_{L\to 0} = \left(\frac{dQ_{exp}}{dL}\right)_{L\to 0} V_i$$

where Q_{exp} is the experimental heat released, L is the mixing-cup length, t is time, $(dQ_{exp}/dL)_{L\to 0}$ is the gradient of the heat release with with cup length at zero, and $(dL/dt)_{L\to 0}$ is the injection velocity (V_i). Values of $(dQ_{exp}/dL)_{L\to 0}$ expressed in kcal/(ft)(mole acid) were obtained at each pressure from the curves of figure 4(a), while injection veloc- ities were obtained from figure 3. The variation of $dQ_{exp}/dt_{L\to 0}$ (hereinafter called the heat-release rate) with injection pressure or velocity is shown in figure 6. The two fuels gave heat-release-rate curves of similar shape. The abrupt increase in slope indicates the existence of a critical injection velocity or pressure whose value is about the same for each fuel.

A possible explanation of the behavior of these curves may be obtained from consideration of the following expression for the heat- release rate:

$$\left(\frac{dQ_{exp}}{dt}\right)_{L\to 0} = ke^{-E/RT}F(M)$$

where k is a rate constant (in kcal/(sec) mole acid)), E is the activation energy for the reaction, R is the universal gas constant, T is temperature, and $F(M)$ is the fraction of total propellant that is mixed. It is assumed that mixing occurs in the interfacial surfaces between fuel and acid and thus the fraction of material mixed will increase with interfacial area. Previous studies with the type of apparatus used in this study have shown that mixing increases with flow velocity (ref. 8).
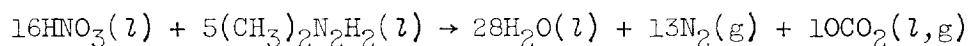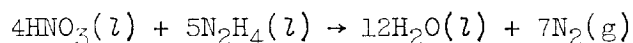
The increase in heat-release rate with injection velocity at the lower velocities (fig. 6) may thus be attributed to an increase in interfacial area or in $F(M)$. The rapid rise in heat-release rate observed at injection velocities of 120 to 140 feet per second is attributed to an increase in temperature. In this velocity range it appears that heat generated in the interfacial area can no longer be dissipated to the surrounding fluid at a sufficient rate, and therefore the temperature of the reacting material increases, which results in an exponential increase in heat-release rate. At velocities greater than about 140 feet per second the heat-release rates attain constant

values or perhaps decrease slightly, which indicates that temperature has attained a constant value. This temperature is probably a characteristic temperature of the propellant system such as the flame temperature. It is possible that gas evolution rates accompanying the reaction are sufficient at the highest injection velocities to inhibit the mixing process. The resulting decrease in F(M) would thus account for a decrease in the heat-release rate.

A comparison of the maximum heat-release rates shows that hydrazine has a rate about 70 percent larger than UDMH. The values are 83,000 and 48,000 kcal/(sec)(mole acid) for hydrazine and UDMH, respectively. In reference 9 it was found that the combustor volume needed for complete combustion of hydrazine was about half that required for UDMH. This result agrees with the relative heat-release rates found for the two fuels.

Correlation of Equilibrium Pressures with Heat-Release Data

The equilibrium pressures shown in figure 5 should correlate with and serve to check the heat-release data. The equilibrium pressure and the bulk of the heat evolved in these experiments appear to be due to the combustion reaction. From the two measurements, pressure and heat release, it was possible to calculate independently two values of the extent of the combustion reaction expressed as the number of moles of acid reacted. The combustion reactions assumed were

$$4HNO_3(l) + 5N_2H_4(l) \rightarrow 12H_2O(l) + 7N_2(g)$$

$$16HNO_3(l) + 5(CH_3)_2N_2H_2(l) \rightarrow 28H_2O(l) + 13N_2(g) + 10CO_2(l,g)$$

Pressures were thus due to nitrogen and a part of the carbon dioxide given by Henry's law. By use of experimental pressures in the ideal gas law for the stoichiometric quantities, it was possible to calculate the moles of acid that had reacted.

To arrive at a comparable value from the heat data requires a determination of that portion of heat due to combustion. In addition to combustion, sources of heat were the neutralization reaction and the heat of solution of unreacted material and products of reactions in the water. Among the products of reaction only a part of the carbon dioxide, given by Henry's law, dissolved in water. Since this was a small amount and the heat of solution is small, this quantity was neglected.

A material balance may be written as follows:

$$X = X_1 + X_2 + X_3$$

$$Y = Y_1 + Y_2 + Y_3$$

where X and Y are the number of moles of acid and fuel injected, respectively, and the subscripts 1, 2, and 3 are the number of moles reacting by combustion, neutralization, and solution, respectively. The number of moles neutralized does not include those that subsequently were combusted.

The heat balance may then be written

$$Q_{exp} = Q_1 X_1 + Q_2 X_2 + Q_3 X_3 + Q_3' Y_3$$

where Q_{exp} is the total heat measured experimentally, Q_1, Q_2, and Q_3 are, respectively, the heats of combustion, neutralization, and solution per mole of acid, and Q_3' is the heat of solution per mole of fuel.

In addition there are several acid-fuel ratios:

$$\text{Input ratio} = \frac{X}{Y}$$

$$\text{Stoichiometric combustion ratio} = \frac{X_1}{Y_1}$$

$$\text{Neutralization ratio} = \frac{X_2}{Y_2}$$

Also, either X_3 or Y_3 is zero depending on the input ratio. For all input ratios studied except one, acid was in excess and $Y_3 = 0$. The single exception occurred at the fuel-rich ratio with hydrazine. The input ratios are tabulated in the preceding section. Values of the various Q's and ratios are given in the following table:

	Q_1, $\dfrac{\text{kcal}}{\text{mole acid}}$	Q_2, $\dfrac{\text{kcal}}{\text{mole acid}}$	Q_3, $\dfrac{\text{kcal}}{\text{mole acid}}$	Q_3', $\dfrac{\text{kcal}}{\text{mole fuel}}$	$\dfrac{X_1}{Y_1}$	$\dfrac{X_2}{Y_2}$
N_2H_4	177	18.5	6.1	3.6	0.8	1.0
UDMH	132	19.0	6.1	---	3.2	1.0

Values of Q_1 were calculated for the stoichiometric quantities given previously, while Q_2 and Q_3 were determined experimentally for the dilute solutions involved in this study; Q_2 thus includes the heat of solution or dilution of neutralization products.

These equations were solved for X_1, the moles of acid reacting by the combustion reaction. Values of X_1 obtained from pressure measurements are plotted against those from calorimetric data in figure 7. A perfect correlation would have resulted in a slope of unity as shown. The agreement found was considered reasonable in view of the possible sources of error in the calculations and in the experimental data.

Suggested Combustion Mechanism

The combustion mechanism postulated for these highly reactive propellant systems under conditions of forced mixing is reaction at fuel-acid interfaces. Provided the interfacial area or mixing is great enough, reaction or heat release appears to proceed at a rate characteristic of the propellants. If the mixing becomes too great, it appears that the heat-release rate may be decreased because of gas evolution that forces the propellants to separate. It is also possible that gas evolution could lead to additional breakup of the fluid to smaller drops. As shown in references 1 and 2, small drops are desirable in a rocket engine because they give the largest conversion rates with propellant systems that are not self-igniting. Further studies are indicated to determine whether there is an appreciable effect of gas evolution on resultant drop size.

The heat-release rates found in this study were compared with approximate rates of convective heat transfer to a burning drop using the expressions of reference 2. For drops of about 100 microns in diameter the two rates were the same order of magnitude. Thus the heat release found in this study is appreciable and could considerably modify the vaporization theory.

SUMMARY OF RESULTS

The liquid-phase heat-release rates of unsymmetrical dimethyl-hydrazine (UDMH) and hydrazine with nitric acid were determined in a bomb calorimeter under conditions of forced mixing. The results may be summarized as follows:

1. The maximum rate of heat release of hydrazine was about 70 percent greater than that of UDMH, the values being 83,000 and 48,000 kcal/(sec)(mole acid) for hydrazine and UDMH, respectively.

8

2. The rate of heat release appears to depend on the interfacial area between the propellants or on the degree of mixing. Above a narrow range of injection velocities representing a critical amount of interfacial area, the rates were almost constant with injection velocity.

3. Within the range mixture ratio was varied it had no effect on the total amount of heat released.

Lewis Research Center
    National Aeronautics and Space Administration
        Cleveland, Ohio, May 31, 1960

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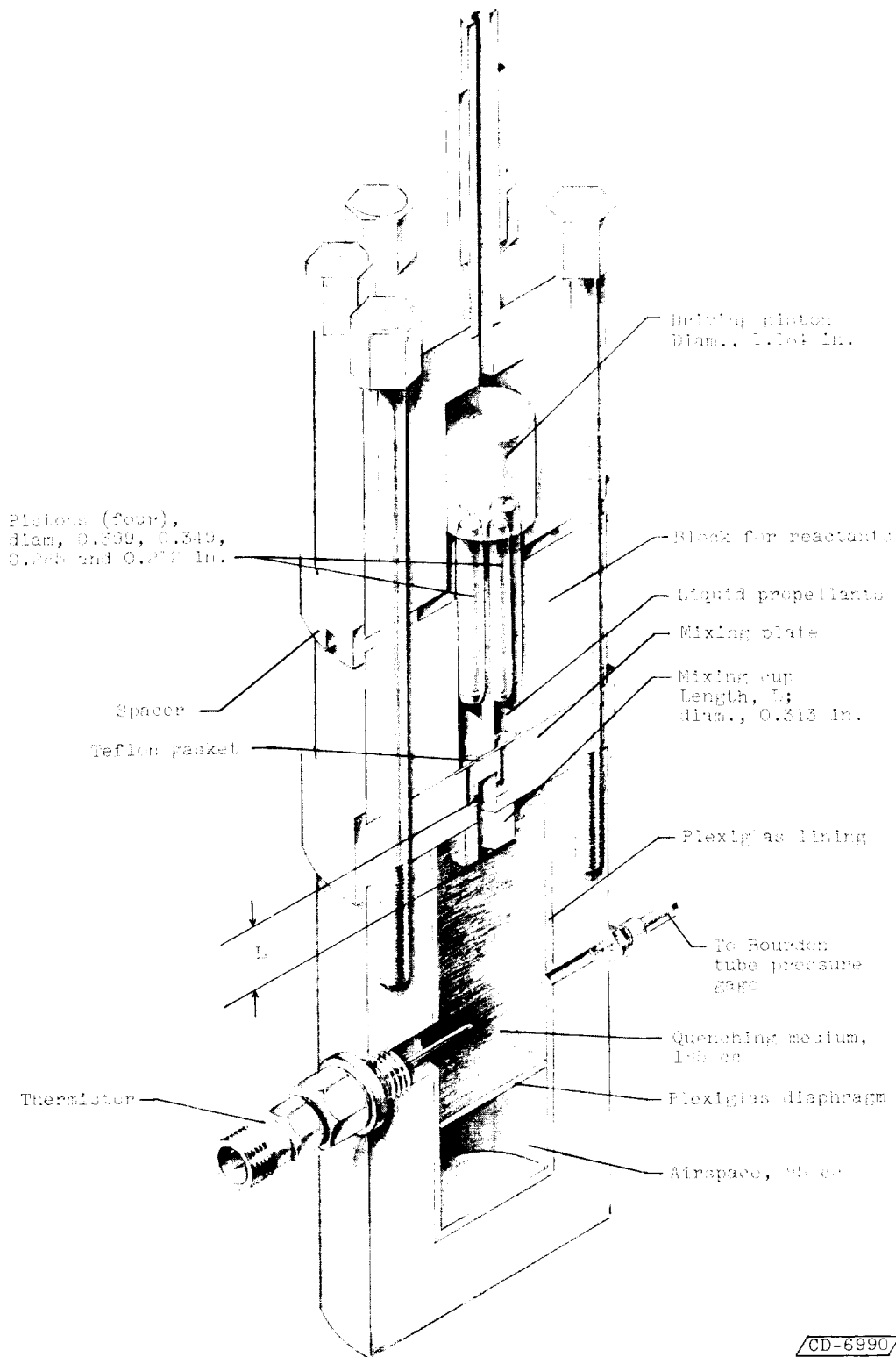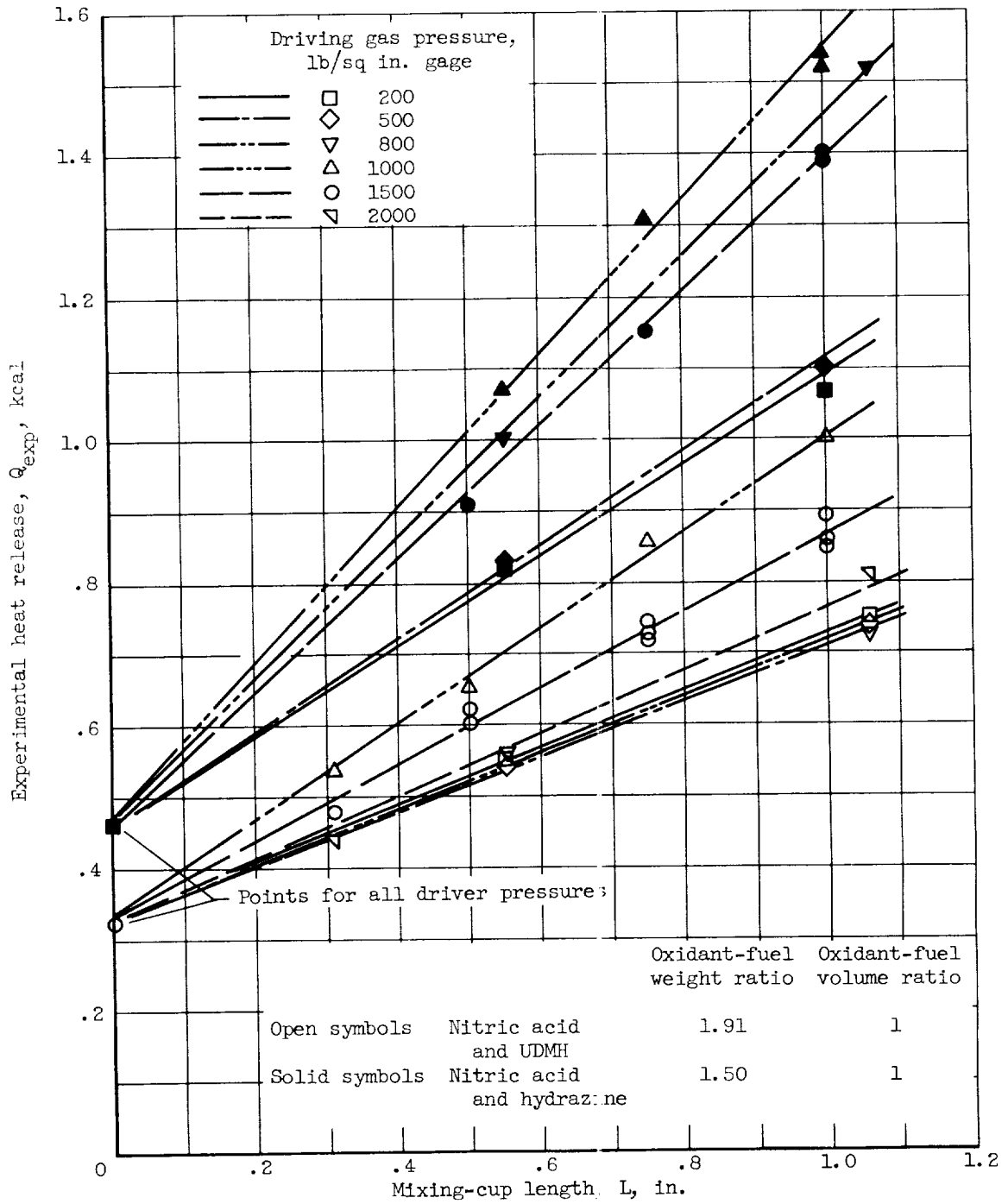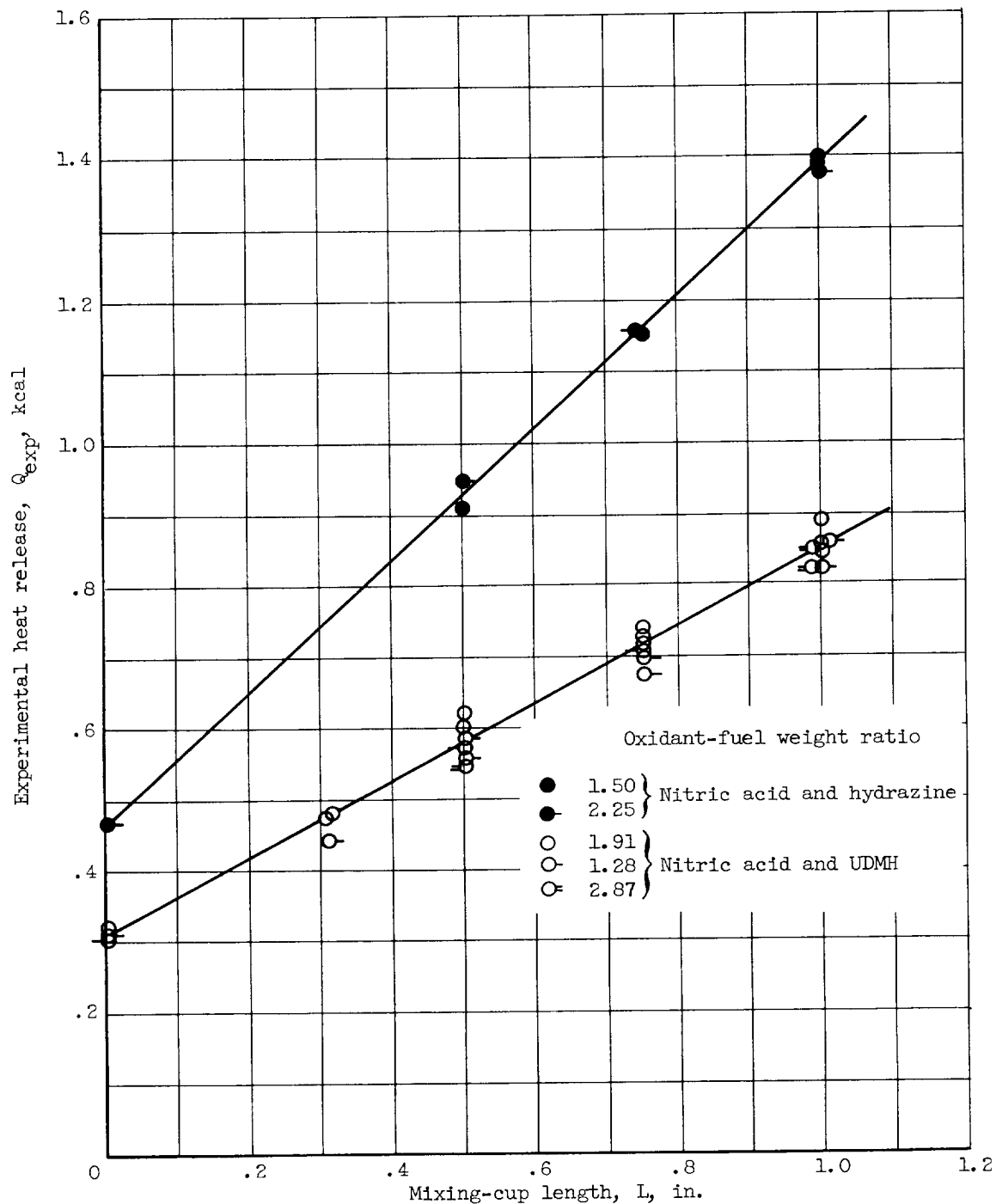9. Feiler, Charles E., and Baker, Louis, Jr.: A Study of Fuel-Nitric Acid Reactivity. NACA RM E56A19, 1956.

Figure 1. - Bomb-calorimeter assembly.

(a) Various driver pressures.

Figure 4. - Experimental heat-release curves.

(b) Various oxidant-fuel ratios. Driving gas pressure, 1500 pounds per square inch gage.

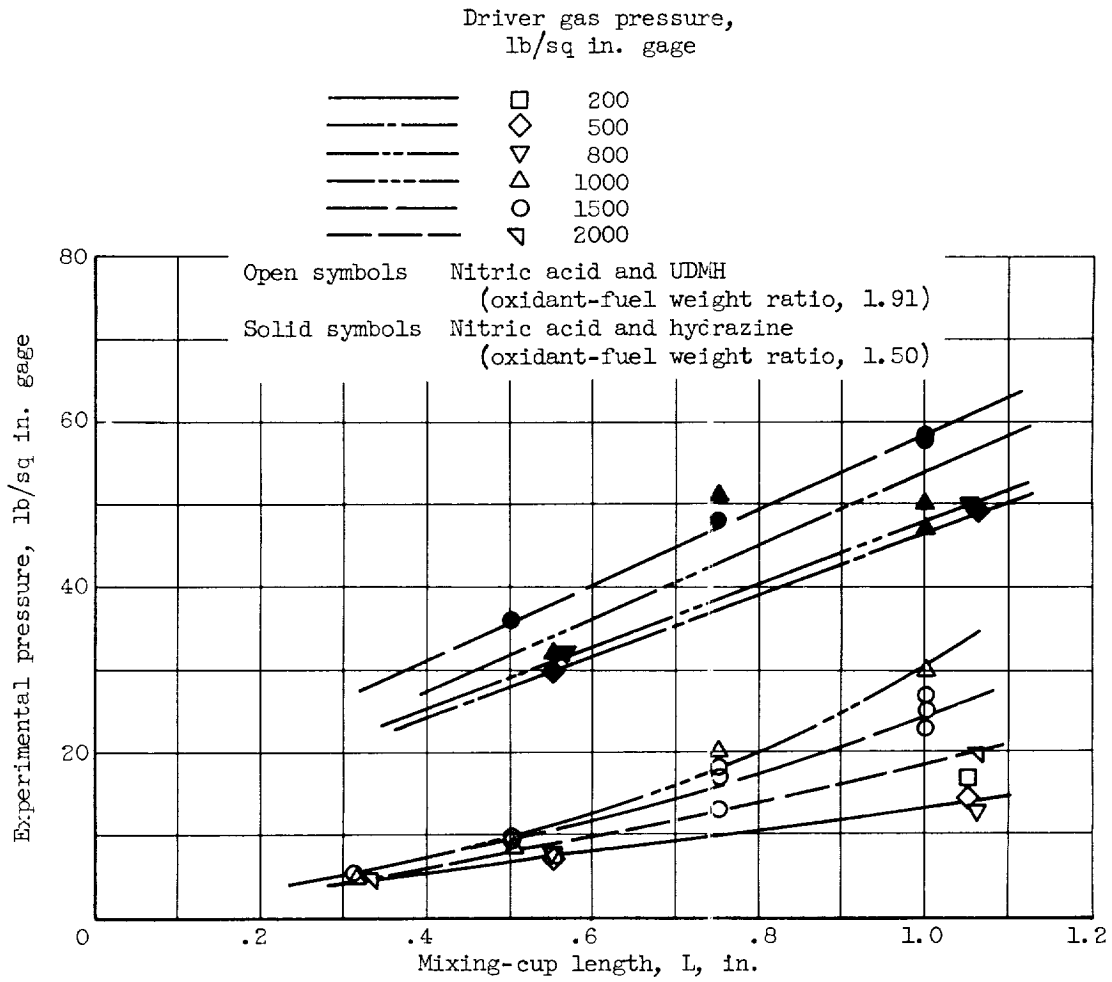Figure 4. - Concluded. Experimental heat-release curves.

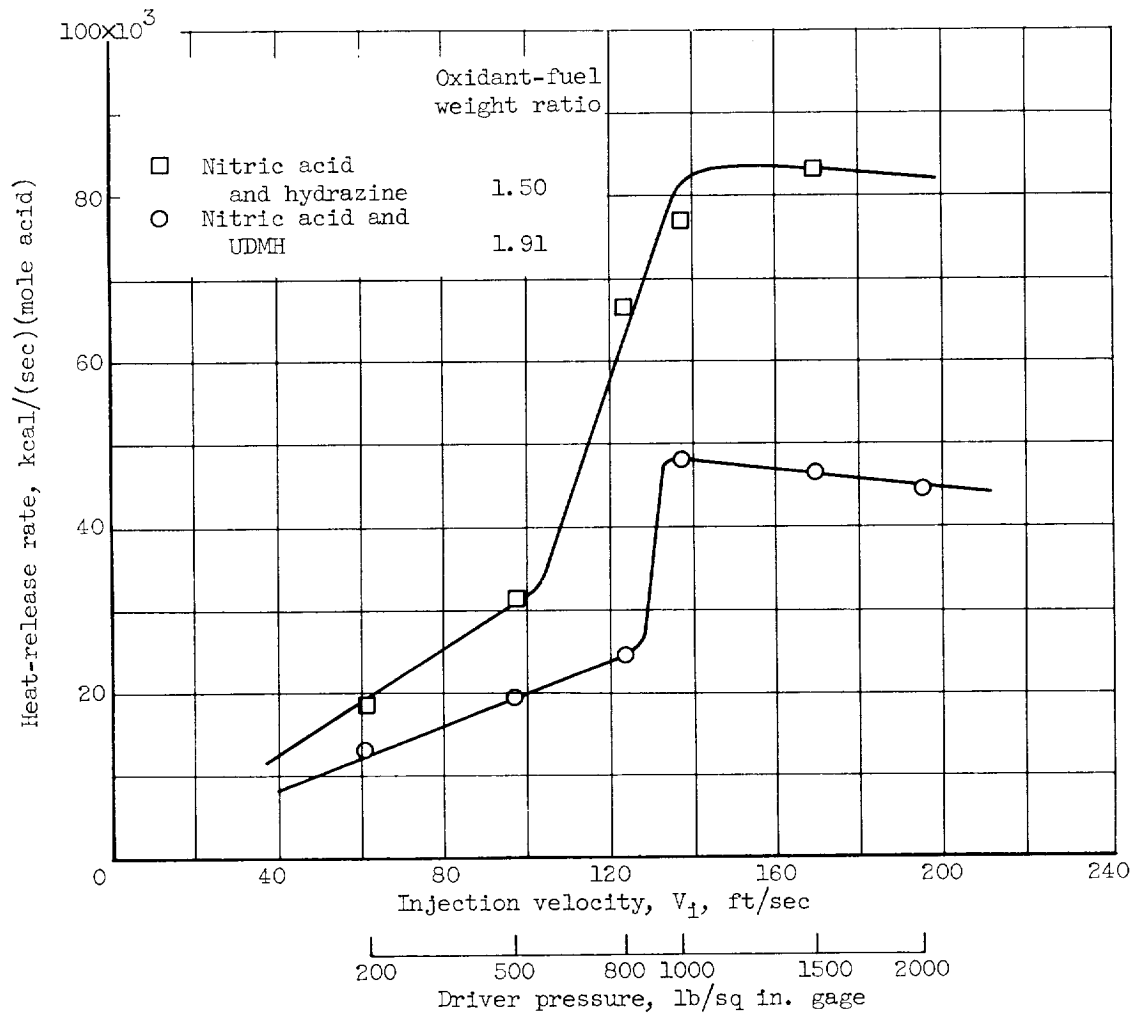Figure 5. - Experimental pressure measurements. Equilibrium conditions.

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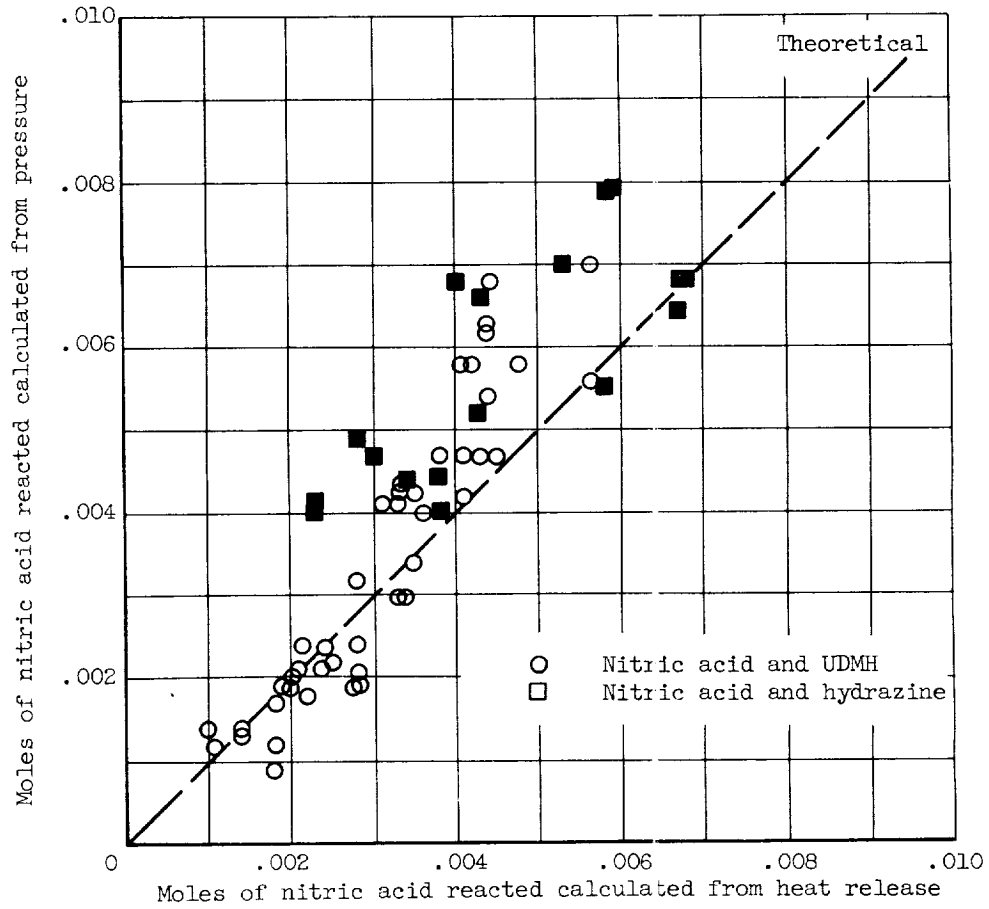Figure 6. - Heat-release rate as function of injection velocity.

Figure 7. - Correlation of heat release with pressure data.