SN-4500

A BASIC STUDY OF THE NITROGEN TETROXIDE-HYDRAZINE REACTION

TECHNICAL REPORT

FACILITY FORM 602

N65-30838
(ACCESSION NUMBER)

56
(PAGES)

CR 64333
(NASA CR OR TMX OR AD NUMBER)

(THRU)

1
(CODE)

06
(CATEGORY)

GPO PRICE $ _____

CSFTI PRICE(S) $ _____

Hard copy (HC) 3.00

Microfiche (MF) .50

ff 653 July 65

Jet Propulsion Laboratory Contract No. BE4-229751

July 1965

DYNAMIC SCIENCE CORPORATION

Bridging the gap between basic research and product production

Chemistry • Physics • Medical Sciences • Structural Mechanics • Gas Dynamics

SN-4500

A BASIC STUDY OF THE NITROGEN TETROXIDE-HYDRAZINE REACTION

TECHNICAL REPORT

Jet Propulsion Laboratory Contract No. BE4-229751

July 1965

NAS 7-100

DYNAMIC SCIENCE CORPORATION
1900 Walker Avenue
Monrovia, California 91016

SN-4500

Prepared for: Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California

Author: Harold G. Weiss, Senior Chemist
Dynamic Science Corporation

Approved: _____

Melvin Gerstein, Ph.D., President
Dynamic Science Corporation

This work was performed at the Dynamic Science Laboratories for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by NASA under Contract NAS7-100. Technical manager for JPL was Mr. David D. Evans.

DYNAMIC SCIENCE CORPORATION
1900 Walker Avenue
Monrovia, California 91016

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF TABLES

I. INTRODUCTION

The nitrogen tetroxide-hydrazine (N_2O_4-N_2H_4) rocket propellant combination exhibits an extremely rapid liquid phase reaction rate. This factor requires the utilization of special injector techniques to accomplish liquid phase mixing since the rapid reaction tends to disrupt the mixing process with a resultant decrease in performance of some injectors. Some attempts were made to physically increase the mixing of a doublet element by the Jet Propulsion Laboratory[1]. Since these physical methods were unsuccessful, it was decided to attempt to find a chemical inhibitor for the N_2O_4-N_2H_4 reaction[2]. Such an inhibitor presumably would allow mixing to be accomplished before sufficient energy could be released to disrupt the impingement process. To summarize, it was found that the ignition delay time could be varied over a range of 0.8 to 4.2 milliseconds by the use of additives to the fuel including such compounds a fluorobenzene and triethylborate (the value for the delay time without inhibitors was 2.6 milliseconds). However, it was found that these inhibitors had little effect on the mixing process when subjected to rocket engine testing in the 2000-lb. thrust standard test engine at JPL; experimental combustion efficiency remained unchanged from the case without additives[3].

The decision was then made to pursue this chemical approach further in three phases: Phase I being to determine the temperature, and to measure the heat evolved in the first step of the nitrogen tetroxide-hydrazine reaction through the use of differential thermal analysis techniques; Phase II

being to examine the infrared spectrum of any solid phase thus formed in order to identify any intermediate species which may be present in the reaction; and Phase III being to determine the effects of various surface-active agents on the miscibility of N_2O_4-N_2H_4 by photographing the dropwise addition of the oxidizer into the fuel. This report contains the results of the investigations performed in the three phases described above.

II. EXPERIMENTAL PROGRAM

A. INFRARED TECHNIQUES

Low temperature infrared spectra were obtained in a specially constructed low temperature infrared cell which is shown in Figure 1. A sodium chloride window (A) was secured in a hollow copper mount (B), the window was cooled by placing liquid nitrogen or Freon refrigerant inside the copper mount (C). Temperature of the window was measured using a Leeds & Northrup K-3 potentiometer to record the output from a copper-constantan thermocouple; the later was cemented to the back of the window with glyptal cement. Care was taken that a minimum of glyptal was used so that no contamination of the recorded spectrum was obtained.

The cell mount assembly was attached to a 45/50 standard taper ground joint (D) so that it could be rotated in line with the fill tube (E) for loading and the cell windows (F) for recording spectra. A glass tube (G) with magnet attached and fitting closely to the fill line could be moved axially along the fill line with an external magnet. Before loading the cell the movable tube was moved close to the cell window. Thus, loss of material on the cold copper was avoided, and both N_2O_4 and N_2H_4 deposition was closely limited to an exact location on the window. After loading the cell, the movable extension tube was again retracted, thus permitting the window and deposited materials to be rotated into the beam of the infrared spectrophotometer. The initial experiments were aimed at learning how much material was required to give a spectrum of optimum intensity.

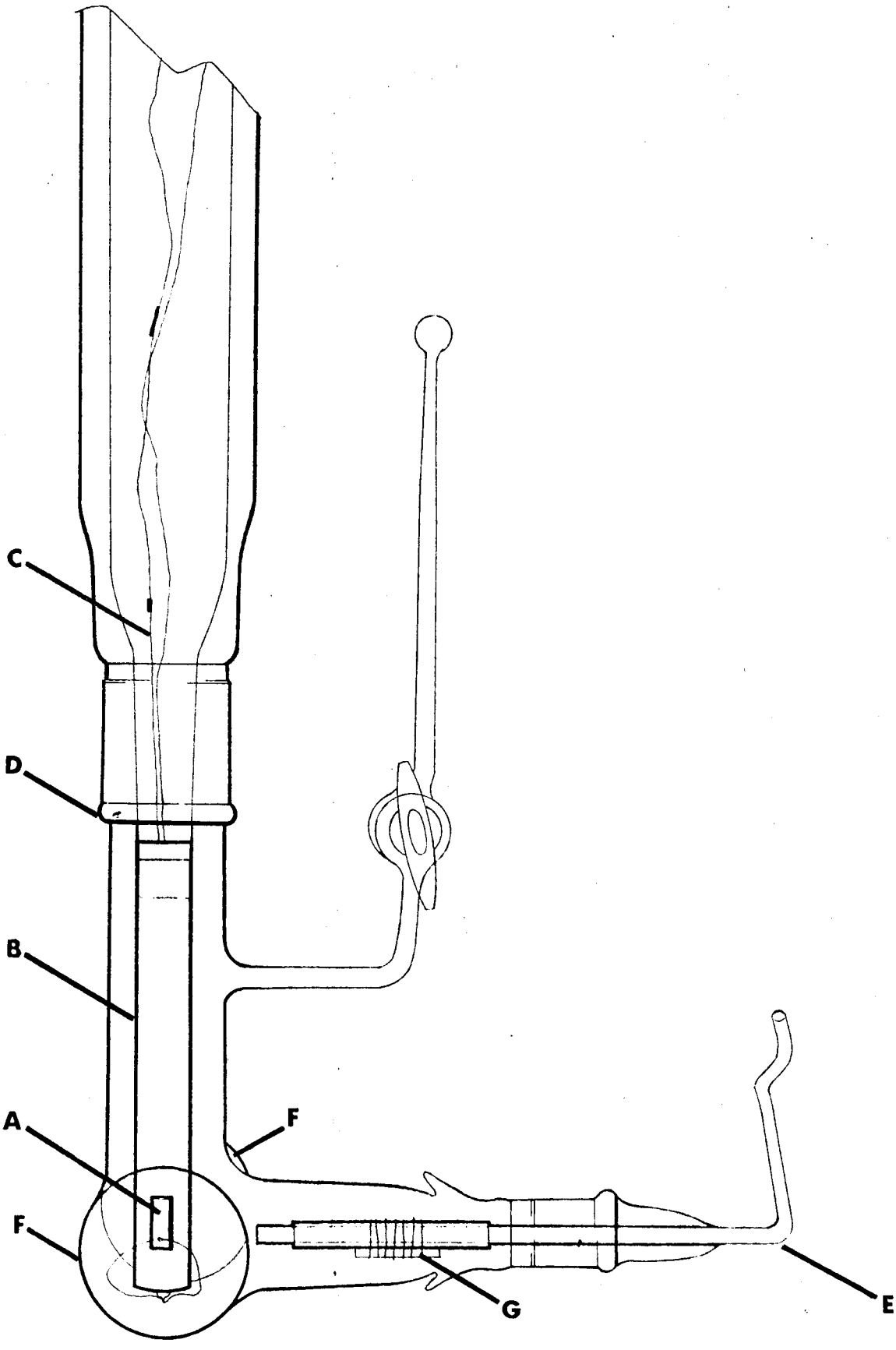


FIGURE 1. LOW TEMPERATURE INFRARED CELL

It was desired that the strong peaks in the spectrum have an absorbance in the range of 0.30 to 0.70, so that changes in intensity of one or more peaks could be observed readily. To illustrate this point two spectra of N_2O_4 are shown in Figures 2 and 3. In Figure 2 only a small amount of N_2O_4 is present, and therefore only the strong spectral peaks appear; thus, changes in the spectra which might affect minor peaks would not be noticed. In Figure 3, too much material is present and therefore changes affecting the strong peaks (which in this spectrum are off scale) would not be recognized. In connection with these spectra, it is interesting to note that the material at -196°C is principally N_2O_4, even though deposited from the vapor phase where appreciable NO_2 is present. In Figure 3 a peak, possibly from NO_2 is present at 1675 cm^{-1}. Actually this peak is very small compared with the N_2O_4 peaks, and represents a low NO_2 concentration. Table I shows the correlation of the spectra from Figures 2 and 3 with literature values.

Upon warming the cells to remove the N_2O_4 a residual, non-volatile material was found on the cell window. The spectrum of this material, which corresponds to sodium nitrate ($NaNO_3$), is shown in Figure 4. This reaction occurred at room temperature (or thereabouts) and did not interfere with reaction spectra.

Calibration runs were also made using hydrazine. A typical spectrum is shown in Figure 5, and is compared with published values in Table II. The small differences may be due to condition of state, since published values are for the gas and the spectrum in Figure 5 is from the solid.

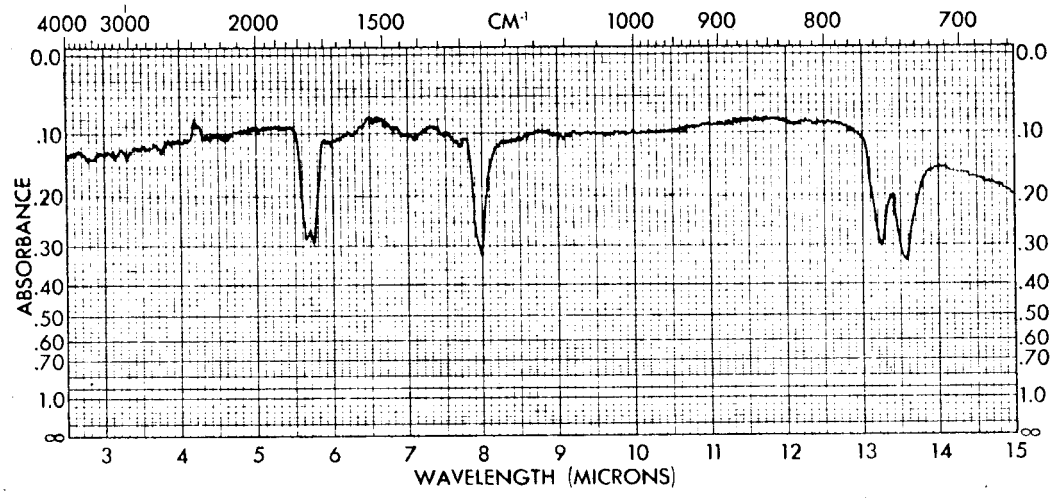


FIGURE 2. INFRARED SPECTRUM OF N_2O_4 (LOW CONCENTRATION) AT -196° C

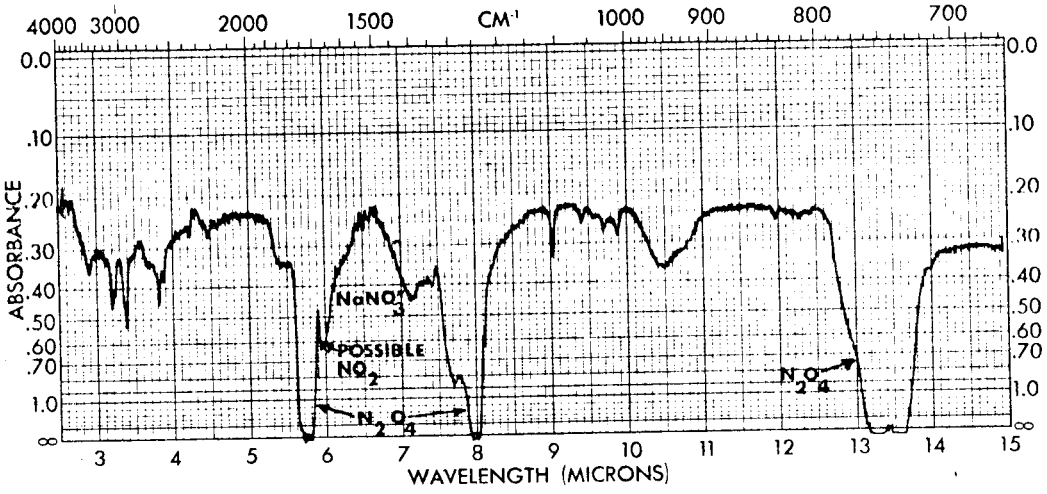


FIGURE 3. INFRARED SPECTRUM OF N_2O_4 (HIGH CONCETRATION) AT -196° C

Table I. Infrared Spectrum

Nitrogen Dioxide and Nitrogen Tetroxide

Frequency (cm^{-1})	Published Spectra* NO_2 gas	NO_2 solid	N_2O_4	(Frequency cm^{-1}) Fig. 3	Fig. 4 (principal peaks)
672			x	738	736
750	x	x	x	757	750
808			x		
1262			x	1256	1250
1318	x				
1380			x		
1618	x				
1624		x			
1712			x	1744	1740
1748			x	1772	

*Kazuo Nakamoto. "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York. p. 83, 100 (1963)

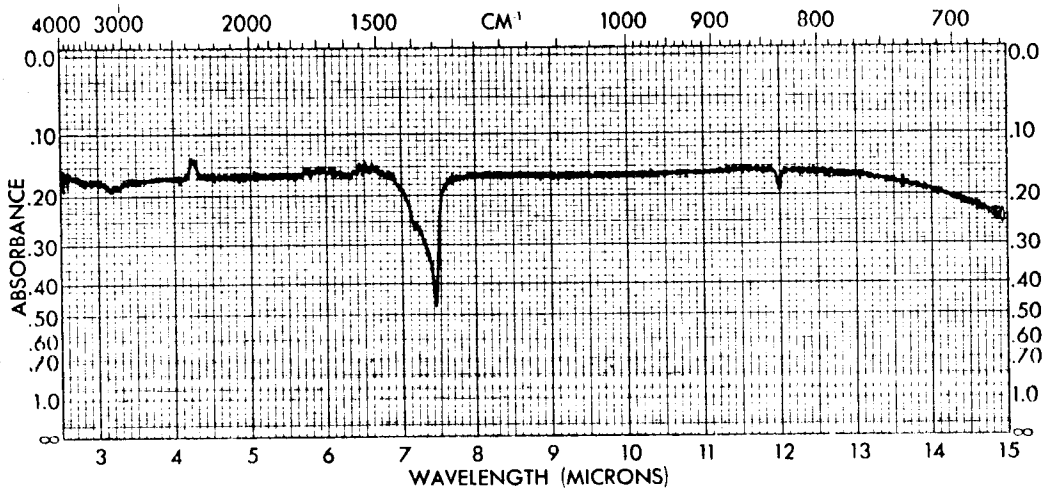


FIGURE 4. INFRARED SPECTRUM OF N_2O_4 RESIDUE ($NaNO_3$)

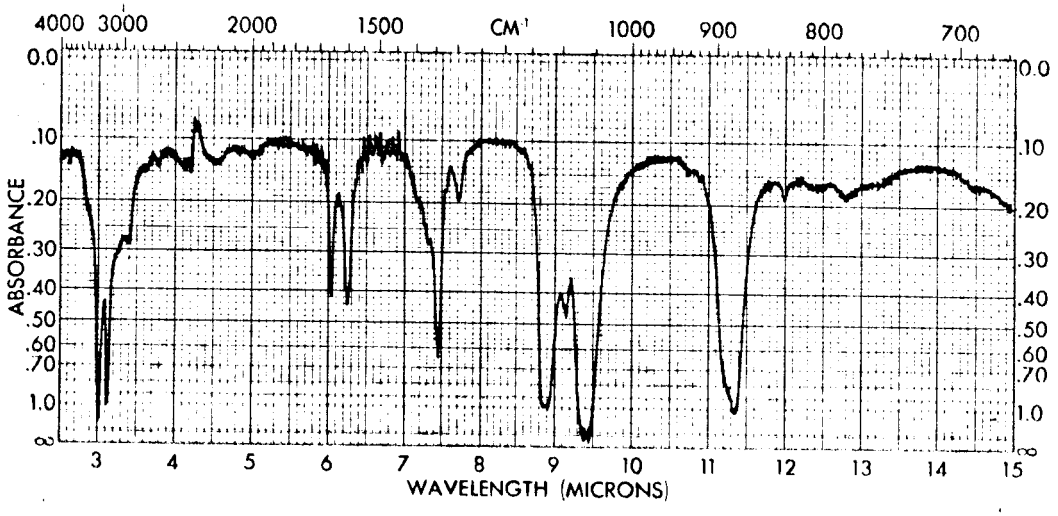


FIGURE 5. INFRARED SPECTRUM OF HYDRAZINE AT -196° C

Table II. Infrared Spectrum of Hydrazine

Published Spectrum* Frequency (cm^{-1})	DSC Spectrum Figure 5 (Frequency cm^{-1})
780	752
933	891
966	1064
1098	1132
1275	1297
1493	1342
1587	1602
1628	1650
3280	3215
3325	3322
3350	

*Kazuo Nakamoto. "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc. New York. p. 83, 100 (1963)

Infrared spectra of nitrogen tetroxide-hydrazine mixtures were obtained at low temperatures. A total of about one hundred and fifty spectra were taken in a series of experiments aimed at distinguishing the minimum reaction temperature and identifying intermediates and products of the reaction. In the procedure used on these experiments, N_2O_4 and N_2H_4 were first condensed on the sodium chloride window at liquid nitrogen temperatures ($-196^{\circ}C$), and then were warmed slowly as spectra were recorded in rapid succession.

Initial experiments indicated reaction taking place at liquid nitrogen temperature. Since this appeared to be unreasonable, the infrared cell was modified by the addition of a thermocouple so that direct measurement of the temperature of the window could be made. Temperature measurements on the window indicated that longer cooling times (than previously used) were required to cool the window to liquid nitrogen temperature. In addition, it was found that even at this low temperature reaction could occur if the hydrazine was deposited too rapidly. Slow transfer of hydrazine to the window was achieved by freezing the N_2H_4 in a liquid nitrogen trap and allowing the transfer to occur as the trap warmed slowly in air. Composite spectra of N_2O_4-N_2H_4 mixtures then were obtained at $-196^{\circ}C$ without apparent reaction.

Two methods were used to warm the mixture in the cell. In the first method, cold nitrogen gas was used to expel the liquid nitrogen from the cell and to flush the cell as it warmed. The rate of warming under the above conditions was six degrees per minute. The rate of warming was reduced to

two degrees per minute by adding Freon, cooled to -155°C, to the cell immediately after the removal of the liquid nitrogen. This latter rate proved satisfactory and was the rate used to obtain the spectra shown in this report.

In a given experiment, the cell window was polished prior to the run, and a blank spectral run was made to insure the absence of contaminants. The N_2O_4 was first deposited and the spectrum recorded. The hydrazine then was transferred and the composite spectrum recorded at liquid nitrogen temperature. A typical composite is given in Figure 6. The peaks have been marked to indicate their origin.

B. GAS ANALYSIS

In conjunction with the low temperature experiments, it was desired to collect, measure and identify the volatile materials of the reaction at various temperatures. The system used to accomplish this is shown in Figure 7. Nitrogen tetroxide and hydrazine were condensed into the reactor at -196°C in a manner identical with that used in the infrared study. The mixture was warmed to -155°C using a Freon bath, and liquid nitrogen was placed on the trap between the reactor and Toepler pump. First, non-condensable gases were measured in the calibrated gas buret, then these were removed and the materials from the trap were transferred and measured. These materials were then removed and analyzed by gas chromatographic analysis. NO_2 and N_2O were separated on a silica gel column maintained at 0°C in an ice bath. Retention times of one and eight minutes were obtained respectively for the two compounds. NO was measured in the non-condensable

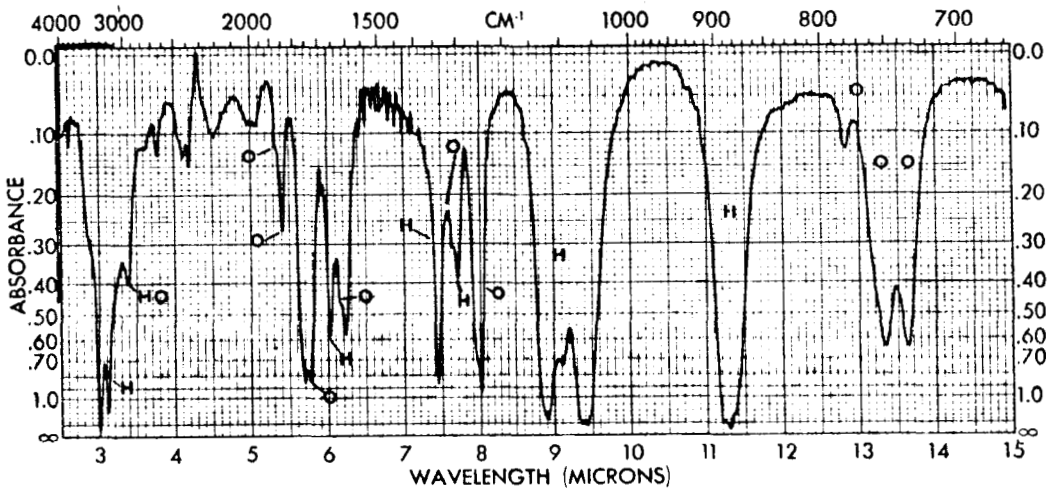


FIGURE 6. COMPOSITE N_2O_4 - N_2H_4 INFRARED SPECTRUM AT - 196° C

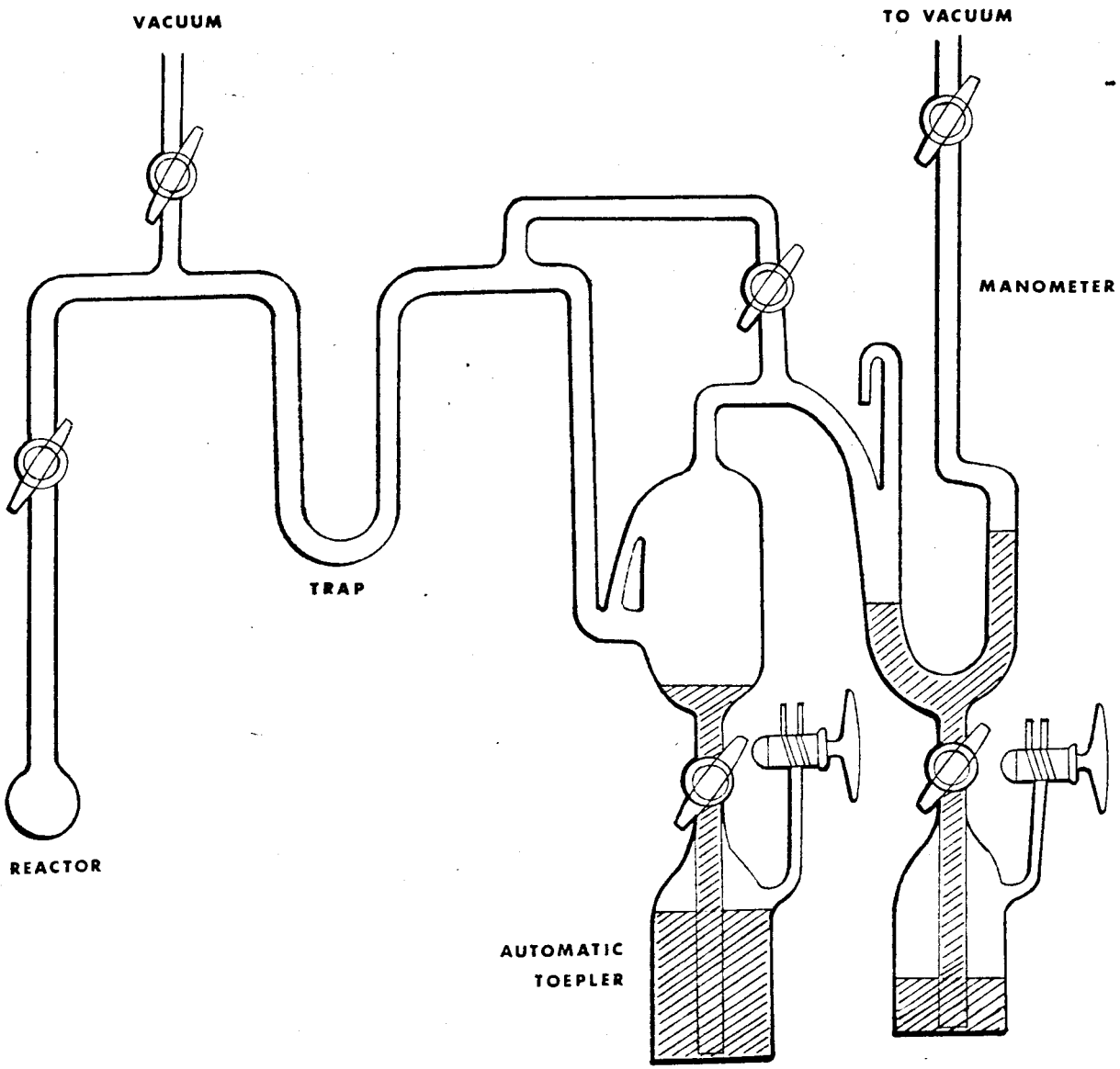


FIGURE 7. DIAGRAM OF SYSTEM FOR MEASURING GASEOUS PRODUCTS OF REACTION

fraction, since it has sufficient vapor pressure at -196°C to be pumped through the liquid nitrogen-cooled trap.

The reactor temperature was increased in steps to -126°, -50°, -30°, and 25°C and the above procedures repeated at each temperature.

C. THERMOCHEMISTRY

Differential thermal analysis of the N_2O_4-N_2H_4 reaction system was made using the apparatus shown in Figure 8. The reaction was run in an all glass system in which the reactor and reference bulb were immersed in the same low-temperature environment. The temperature of the calorimeter was controlled by bubbling nitrogen gas through liquid nitrogen and then into the calorimeter. An electrical heater on the inlet tube allowed the cold nitrogen to be warmed at a uniform rate. The thin reactor and reference bulb were plated with a platinum film and the thermocouples soldered to the surface of the glass to insure intimate contact. In a typical experiment measured quantities of reactants were condensed into the reactor with liquid nitrogen. The liquid nitrogen was dumped out of the dewar and the cold dewar replaced quickly. The flow of cold nitrogen gas was started immediately. Temperature of the reactor and differential between the reactor and reference cell were measured on a potentiometer. The current on the heater winding was increased slowly as required to obtain the desired increase in temperature.

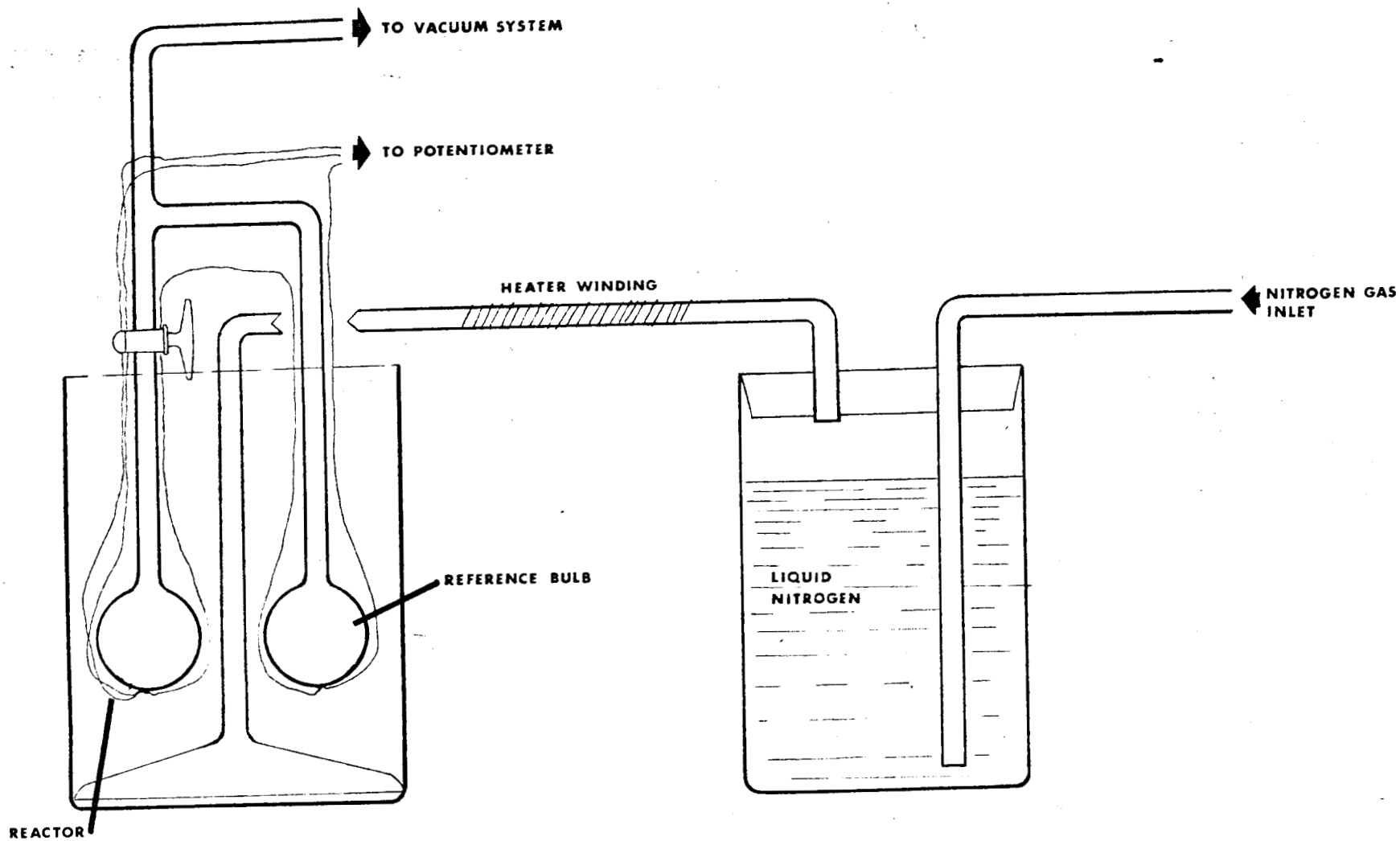


FIGURE 8. DIAGRAM OF D. T. A. APPARATUS

D. MISCIBILITY EXPERIMENTS

High speed motion pictures were taken of the dropwise addition of N_2O_4 to hydrazine, with and without additives. The purpose of these experiments was to find a miscibility agent for the two propellants. The technique of Weiss and Klusmann[4] was used. The procedure involved the use of a fastex camera operating at 4000 to 5000 frames per second to photograph the N_2O_4 drop as it fell through a one-inch column of hydrazine. The apparatus utilized a condenser system of lenses for back-lighting the sample tube. The yellow color defined the N_2O_4 drop which was easily distinguished on color film.

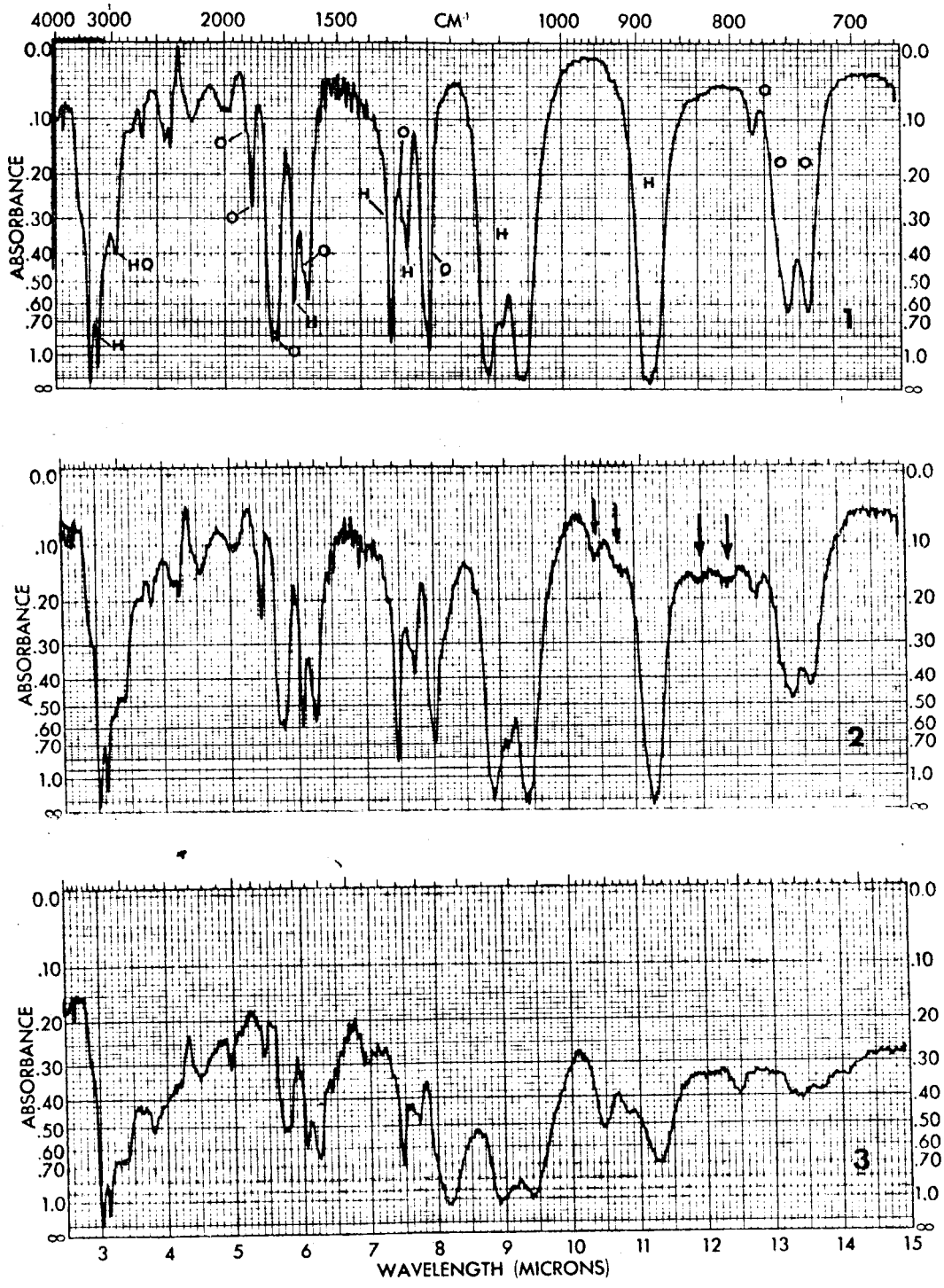
This method also provided a qualitative measure of the reactivity of the propellants.

III. RESULTS AND DISCUSSION

A. THE N_2O_4-N_2H_4 REACTION

The infrared spectrum of the nitrogen tetroxide-hydrazine mixture at liquid nitrogen temperature is shown in Trace #1, Figure 9. The peaks have been identified as to their origin, H for hydrazine, and O for nitrogen-tetroxide. It can be seen that all of the major peaks are accounted for as originating from hydrazine or nitrogen-tetroxide*. The other traces, #2 and #3 in Figure 9, and #4 and #5 in Figure 9a, show the progress of the reaction as the temperature increased. The temperatures given in the figures is the recorded temperature at the beginning and end of each spectral run. Other traces were obtained at intermediate temperatures, but those shown in Figures 9 and 9a were selected since they show the principal steps in the reaction. When the liquid nitrogen was first removed from the cell and Freon coolant was added, I.R. traces were obtained at -150° and $-136^{\circ}C$. At these temperatures the amount of N_2O_4 decreased slightly relative to N_2H_4; however, no new spectral lines were observed. The first evidence of new peaks was obtained in the run at -133° to $-124^{\circ}C$, Figure 9, Trace #2. The new peaks are indicated by arrows. Further progressive changes were evident in spectra up to a temperature of $-43^{\circ}C$, Figure 9a, Trace #5. No further spectral changes were noted at temperatures below room temperature,

*In addition to the fact that all of the peaks are accounted as coming from either N_2O_4 or N_2H_4, the spectrum has also been found not to be missing any peaks normally found in the spectra of these two substances.



H - HYDRAZINE, O - NITROGEN TETROXIDE

FIGURE 9. SPECTRAL CHANGES WITH TEMPERATURE FOR A N_2H_4 - N_2O_4 MIXTURE

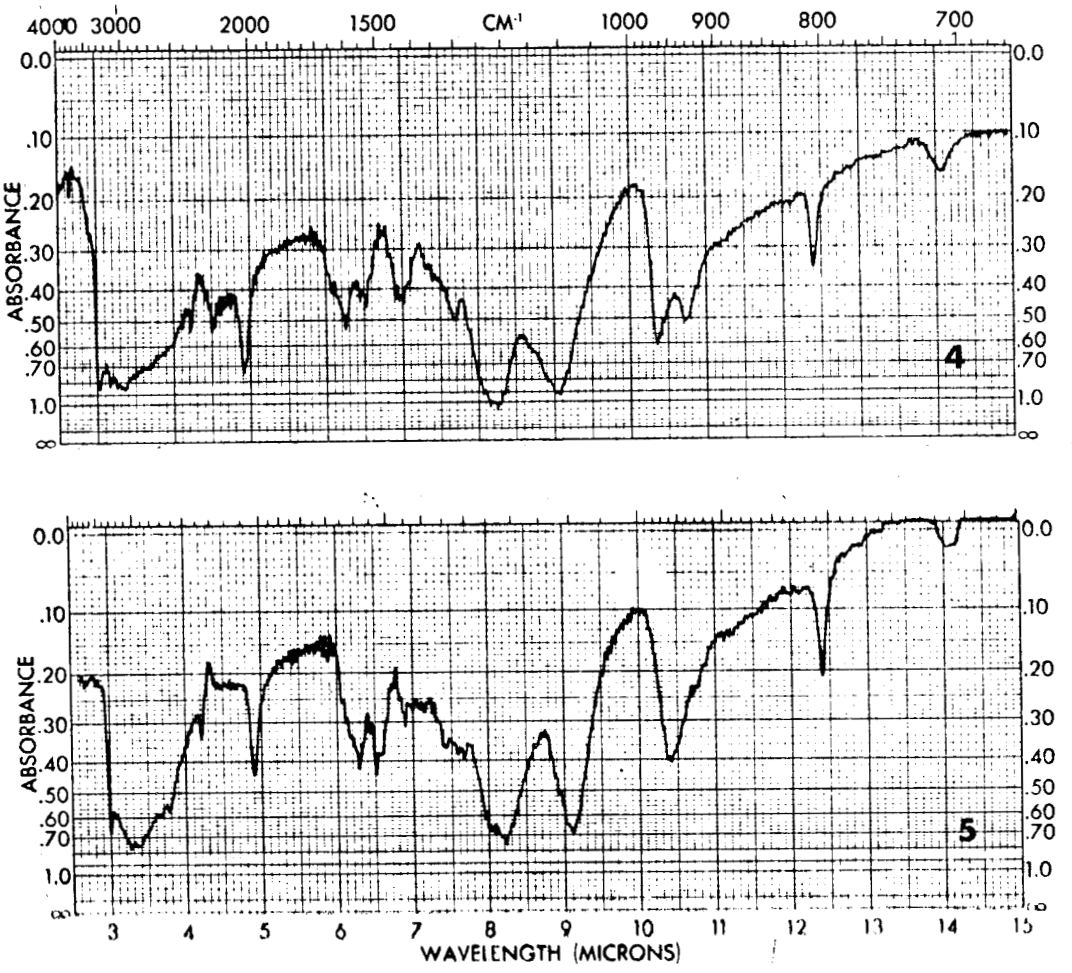


FIGURE 9a. SPECTRAL CHANGES WITH TEMPERATURE FOR A $N_2H_4 - N_2O_4$ MIXTURE

but the overall intensity of the spectrum decreased somewhat. Also, after standing overnight, only sodium nitrate appeared on the spectrum. This material was not present before and was therefore presumably formed by reaction of the N_2O_4-N_2H_4 reaction product with the cell window. A detailed explanation of the spectral changes follows:

The portion of the spectrum from 2.5 to 5 microns is shown in Figure 10. The traces are numbered to correspond to the trace numbers in Figures 9 and 9a. The important part of the spectrum in this region is that between 2.5 and 4 microns. Initial indication of reaction is evidenced by a decrease in intensity of the peak at 3.4 μ (Trace #2). Further evidence of reaction is evident in Traces #3, #4 and #5 by the growth of a broad spectral band in the 3 to 4μ region. This particular region of the spectrum is characteristic of ammonium ion (NH_4^+). It should also be noted that the doublet peak, 3.0 to 3.1 μ in Trace #1 becomes a singlet at 3.0 μ in Trace #5. The doublet is indicative of an $-NH_2$ grouping while the singlet is characteristic of a single -NH vibration.

The 5 to 7 micron region of the spectrum is detailed in Figure 11. Of the peaks appearing in this portion of the spectrum, the doublet at 5.7 - 5.8 μ and the shoulder at 6.18 μ are of interest. It can be shown from gas phase N_2O_4 spectra taken at various pressures* that the 5.7 - 5.8μ doublet is a vibration characteristic of the N_2O_4 molecule while the 6.18μ peak

*The equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ is pressure sensitive, shifting to the left as pressure increases. Thus, the intensity of those peaks due to N_2O_4 should increase, and those of NO_2 decrease, with increased pressure.

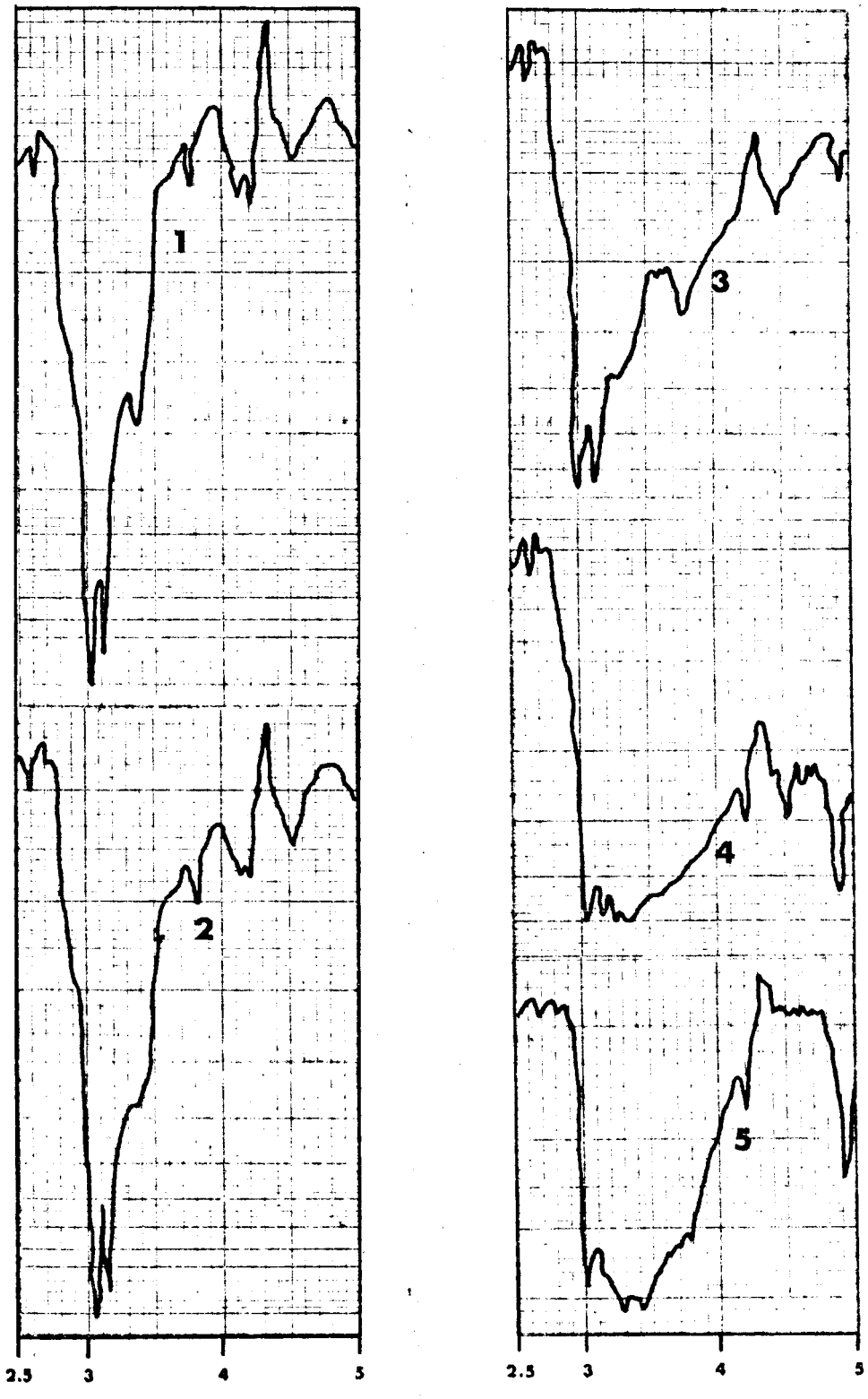


FIGURE 10. ANALYSIS OF SPECTRA IN 2.5 TO 5 MICRON REGION

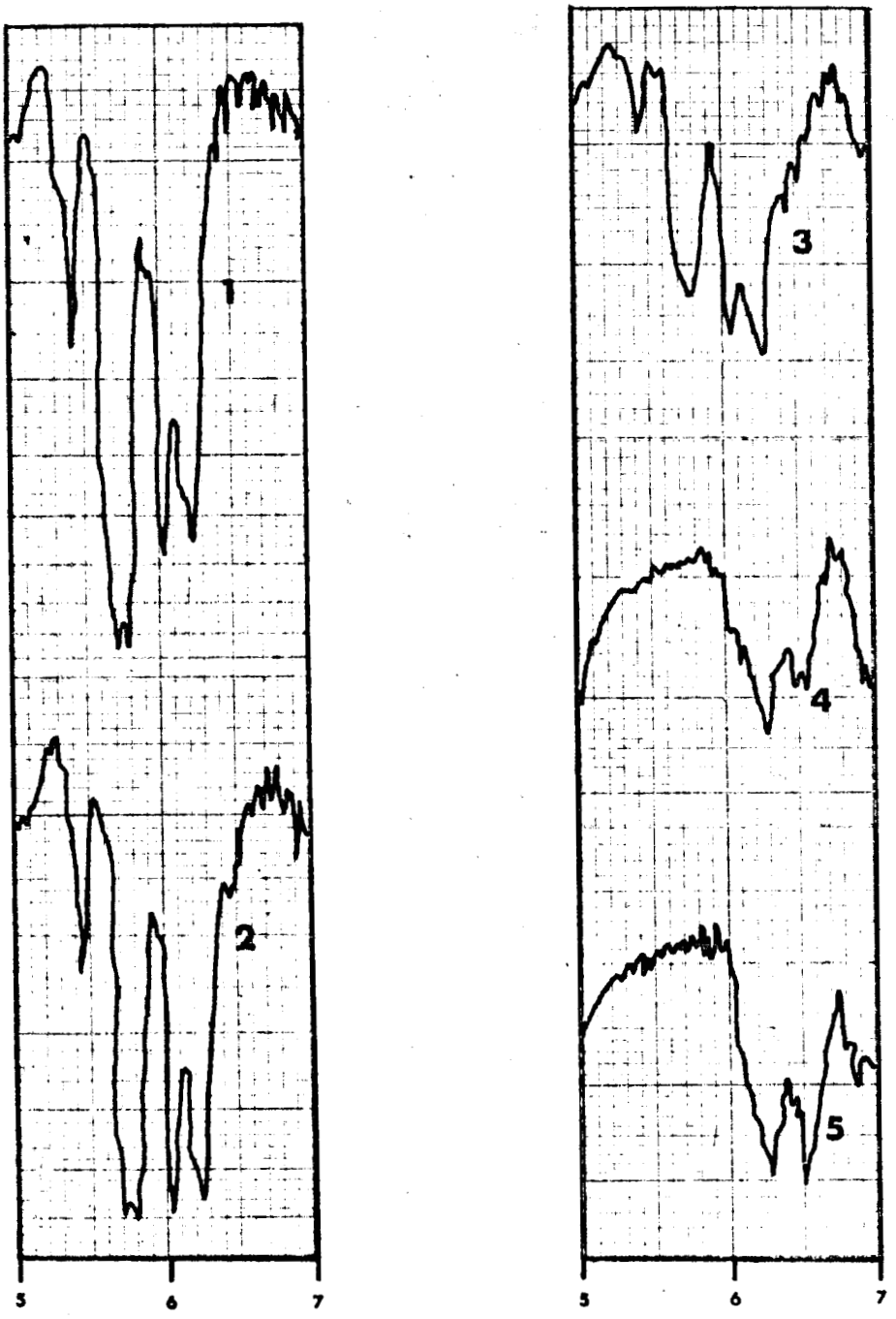


FIGURE 11. ANALYSIS OF SPECTRA IN 5 TO 7 MICRON REGION

belongs to NO_2. Qualitative comparison of Traces #1 and #2 in Figure 11 indicates a more rapid decrease in N_2O_4 than NO_2. Quantitative measurements, which could be made with distinctly separate peaks, are difficult because the NO_2 is hard to separate from the strong hydrazine peaks occurring at 6.03 to 6.22 μ . It can be noted from Traces #4 and #5 in this figure that reaction continues even after all of the N_2O_4 has been consumed. The absence of peaks at 5.7 - 5.8 μ in Trace #4 is evidence of the complete reaction of N_2O_4. The continued growth of the peak at 6.5 μ in Trace #5 is indicative of continuing chemical reaction.

The region of the spectrum from 7 to 10μ (Figure 12) could be used to obtain a measure of the loss of hydrazine if sensitivities for the peak at 7.4 μ could be obtained. The 7.4 μ peak is a region where there is essentially an absence of residue in the final product. In contrast, the hydrazine peaks at 8.9 and 9.4μ could not readily be used on a quantitative basis since the product peak at 9.1 μ interferes. The loss of hydrazine could also be obtained from the 11.3 μ peak given in Figure 13, and the loss of N_2O_4 from the peaks at 13.3 and 13.6μ in Figure 14. In order to make these calibrations the sensitivities (change in peak height with change in concentration) must be obtained for N_2H_4 and N_2O_4 at these frequencies.

Infrared calibration runs were made using the 11.3 μ peak for N_2H_4, and the 13.3 and 13.6 μ peaks for N_2O_4. Gas and liquid phase reactions of both N_2O_4 and N_2H_4 with the NaCl windows prevented standardization by conventional procedures. Therefore, calibrations were made by transferring measured amounts of N_2H_4 and N_2O_4 to the low temperature cell, as would be done in a normal run.

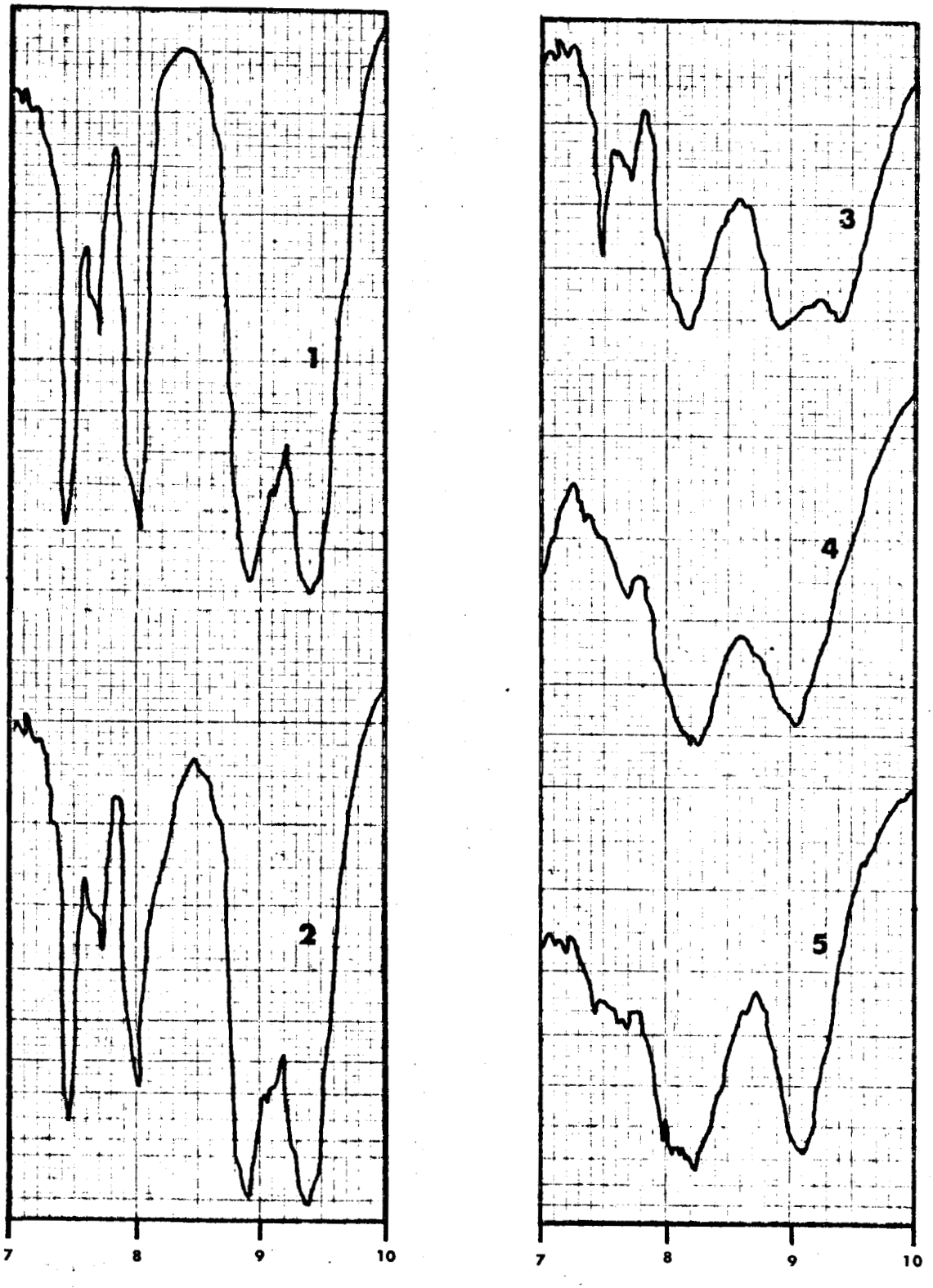


FIGURE 12. ANALYSIS OF SPECTRA IN 7 TO 10 MICRON REGION

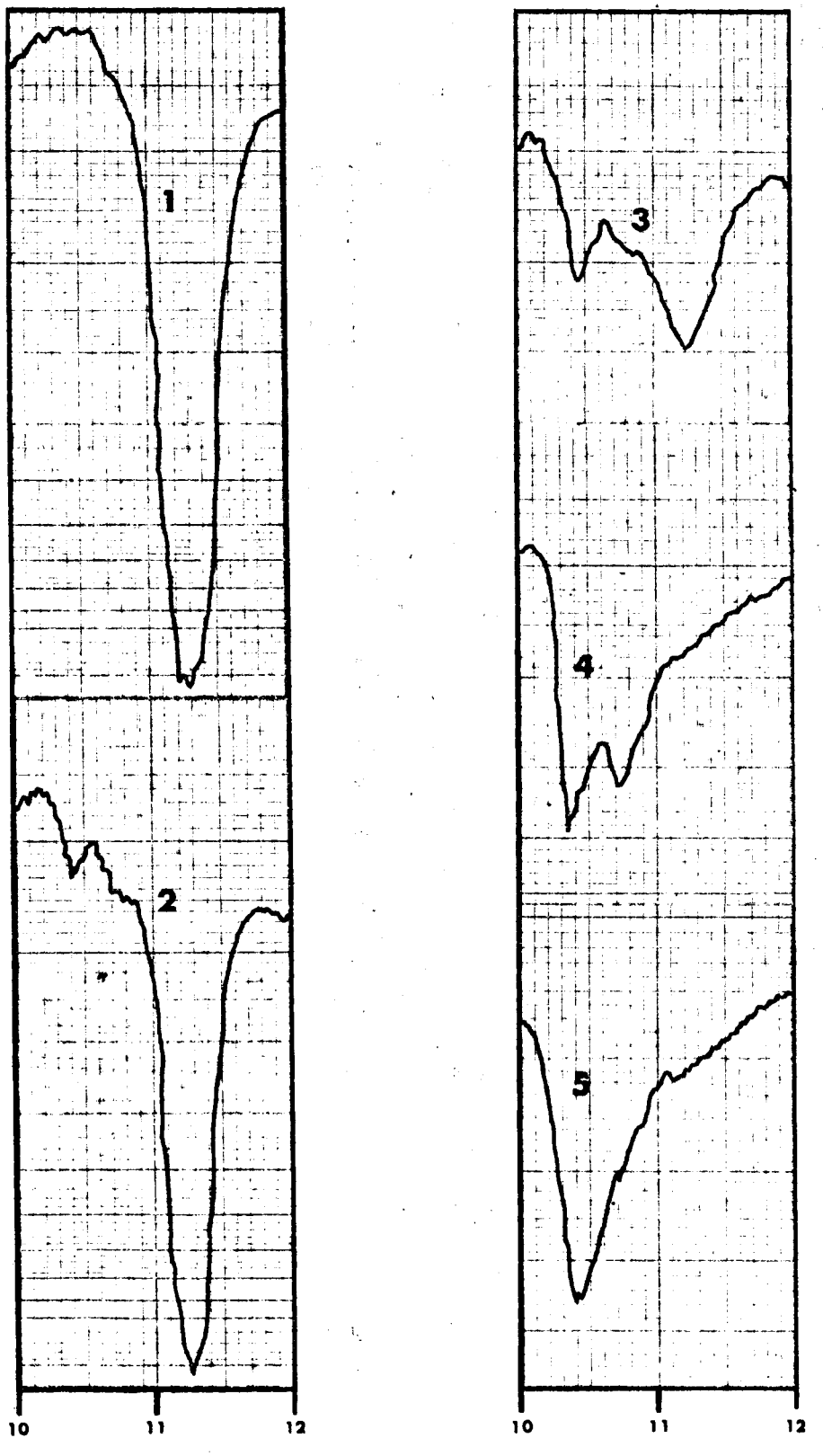


FIGURE 13. ANALYSIS OF SPECTRA IN 10 TO 12 MICRON REGION

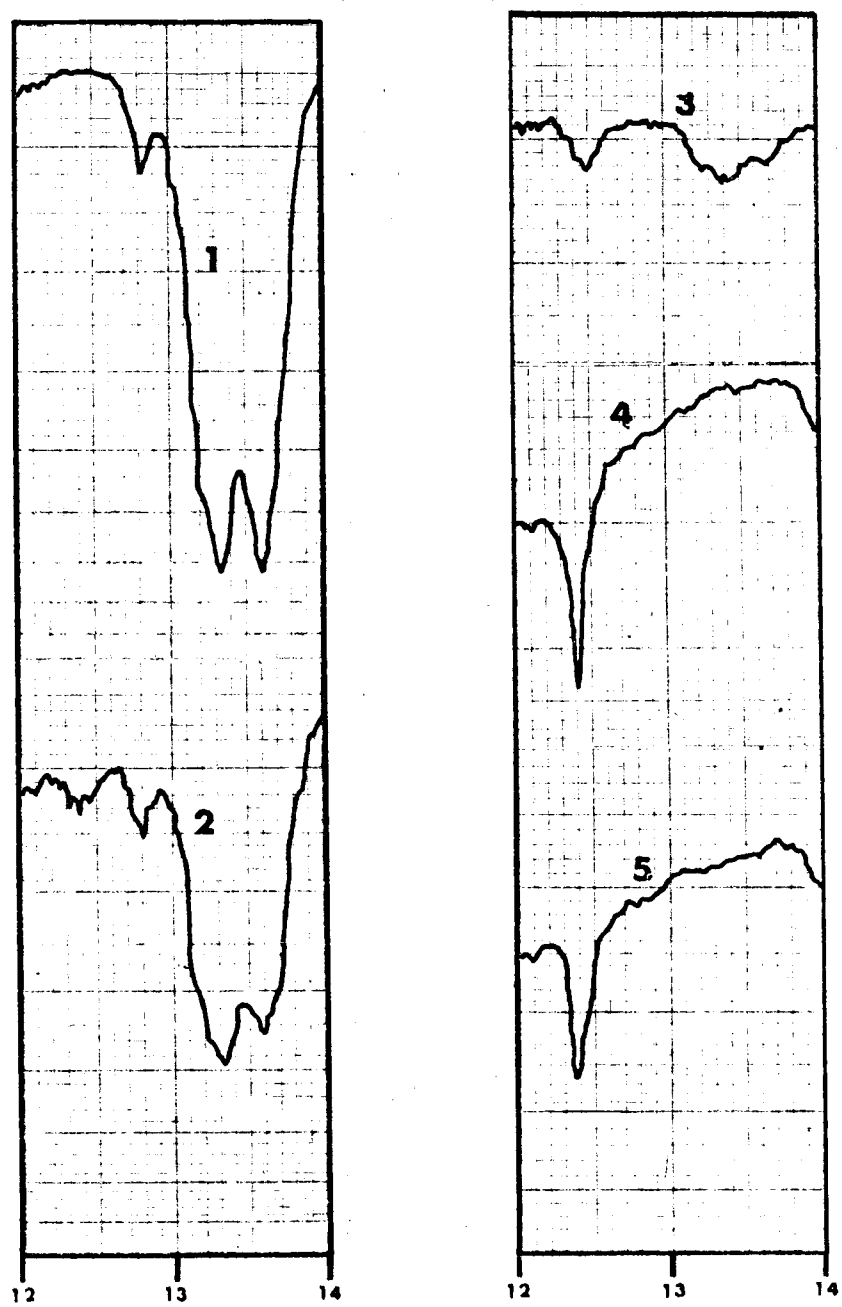


FIGURE 14. ANALYSIS OF SPECTRA IN 12 TO 14 MICRON REGION

Calibration values were used to calculate rate of disappearance of N_2O_4 and N_2H_4 in several runs. No uniform pattern appeared, which could be used with confidence to predict the reacting ratios. This was due, at least in part, to the fact that sensitivities of the two materials varied by a factor of ten. Therefore, the N_2O_4 absorbance in the initial spectrum of each set was very strong, measured changes in this absorption peak were subject to large error.

It was pointed out above that evidence of reaction between N_2O_4 and N_2H_4 could be derived from changes in the infrared spectra at a temperature as low as $-133^{\circ}C$.

In order to establish whether or not this reaction represents adduct formation or reaction it was deemed advisable to measure and identify the volatile gases from the reaction. Of the possible gases that could be obtained, all but ammonia have vapor pressures sufficiently high to be pumped from the reaction system for measurement at $-133^{\circ}C$ where reaction first occurs (see table below). The high sensitivity of the infrared for ammonia insures that it could be observed in the solid phase if it were present.

Compound	Temperature at which Vapor Pressure is:	
	1 mm	10 mm
H_2	-263.3	-261.3
N_2	-226.1	-219.1
NO	-184.5	-178.2
N_2O	-143.4	-128.7
NH_3	-109.1	- 91.9

The reaction was conducted in a glass bulb to which a thermocouple had been attached using glyptal cement. The N_2O_4 and N_2H_4 were condensed in a tube in layers at -196°C. The bulb was then warmed slowly while gases were pumped continuously using a Toepler pump. Gases were pumped into an I.R. cell, where they were measured, and infrared spectra were obtained. The volume of the infrared cell was approximately 30 cc (5 cm path length) and the maximum gas pressure was 5 mm. Therefore, only very small peaks were obtained, these occurring at 4.45, 7.72, and 7.90 μ respectively. The spectrum obtained corresponds to that of nitrous oxide (N_2O), as can be seen from the calibration spectrum shown in Figure 15. The gas from the cell was transferred directly into a mass spectrometer for analysis. A complex spectrum containing obvious hydrocarbon fragments was obtained. It is postulated that NO_2 may have been present and reacted with stopcock grease in the instrument to give rise to the observed spectrum. Quantitative analysis of the spectrum was not possible because of the unknown impurities. The spectrum did show the absence or at most the presence of only very small amounts of NO_2, NH_3 and N_2H_4. The presence of a substantial quantity of N_2O in the product gas was confirmed by a large parent peak at mass 44*. In addition, residual peaks at mass 30 and 28 indicated presence of NO and N_2. The major part of the gas was collected at a temperature above -110°C.

*The mass spectrum of N_2O includes a parent peak at m/e 44, and a fragmentation pattern with major peaks at m/e 30, 28, 16 and 14. All these peaks were present.

More quantitative experiments were conducted in which the non-volatile and volatile products at various temperatures were measured and identified. The results are shown in Table III. The table shows the quantities of gases given off at each temperature, and identifies each gas. Time did not permit accurate measurement of the exact quantity of each gas present at each temperature. However, the gases liberated at each temperature were primarily those shown first in the "Species" column in Table III. Thus, at $-126^{\circ}C$, NO and NO_2 were the primary products of the reaction. It is surprising that such a large quantity of NO_2 was liberated at $-126^{\circ}C$ since the vapor pressure of N_2O_4 at this temperature is so low that one would not expect N_2O_4 to leave the reactor. One possible explanation for this is the formation of an N_2H_4:NO_2 adduct from the N_2O_4-N_2H_4 initial reaction. If this occurred, isolated NO_2 molecules might be pumped from the reactor before combination to N_2O_4 could take place. It is assumed that the NO_2 vapor pressure would, of course, be much higher than that of N_2O_4.

The formation of the large quantity N_2O in the reaction at $50^{\circ}C$ shows that the principal reaction occurs between -126° and $-50^{\circ}C$. This is in agreement with thermochemical data, which will be presented later in this report.

It is of interest that the reactions occurring at temperatures above $-50^{\circ}C$ do not involve additional liberation of gases.

In one of the low-temperature experiments, it was observed that crystals of a solid material had formed in the bulb. A small crystal from

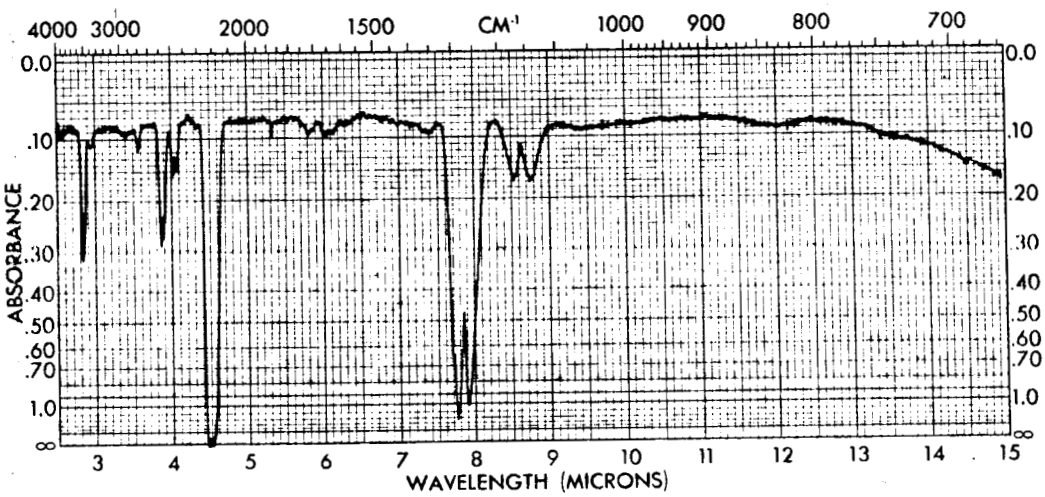


FIGURE 15. INFRARED SPECTRUM OF N_2O GAS

Table III. Gas Evolution from the Low Temperature Reaction of N_2O_4-N_2H_4

Temperature	Gas Evolved (m. moles x 10^{-3})		Species Found
	Noncondensable*	Condensable*	
-126°	.13		NO, N_2
		10.3	NO_2, N_2O
-50°	.52		N_2
		30.5	N_2O, NO_2 + unknown
-30°	.25		N_2
		.27	NO_2
-25°	.02		N_2
		.16	NO_2
Total millimoles Gas Evolved	.92	41.2	

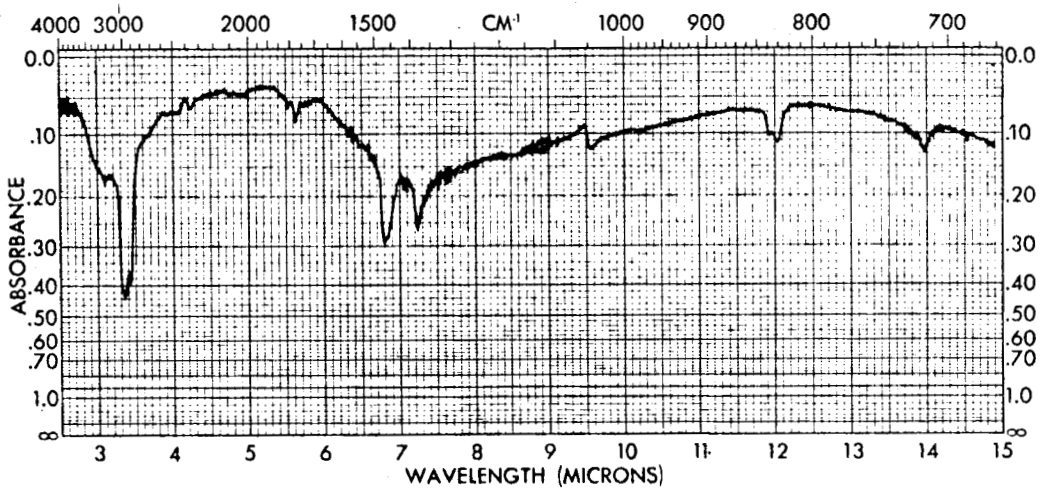
*At $-196^{\circ}C$ in the LN_2 trap

the bulb was sealed into a melting point tube and the melting point was measured. The material melted in the range of 66.3° to 73.0°C. Of the possible products that could be formed in the reaction, only hydrazinium nitrate (m.p. 71°C) fits the observed melting point of the crystals. As a basis for comparison with the observed products in the infrared, the spectra of two possible reaction products ammonium nitrate and hydrazinium nitrate were also obtained. It was necessary to prepare a nujol mull of ammonium nitrate to obtain its spectrum. This spectrum is shown in Trace #1, Figure 16 and the corresponding pure nujol is shown in Trace #2, Figure 16. The true ammonium nitrate spectrum is therefore Trace #1 minus Trace #2, and is represented by three broad bands in the regions of 3, 5.5 and 7 μ and another peak at 12 μ. These peaks are not observed in any of the product spectra.

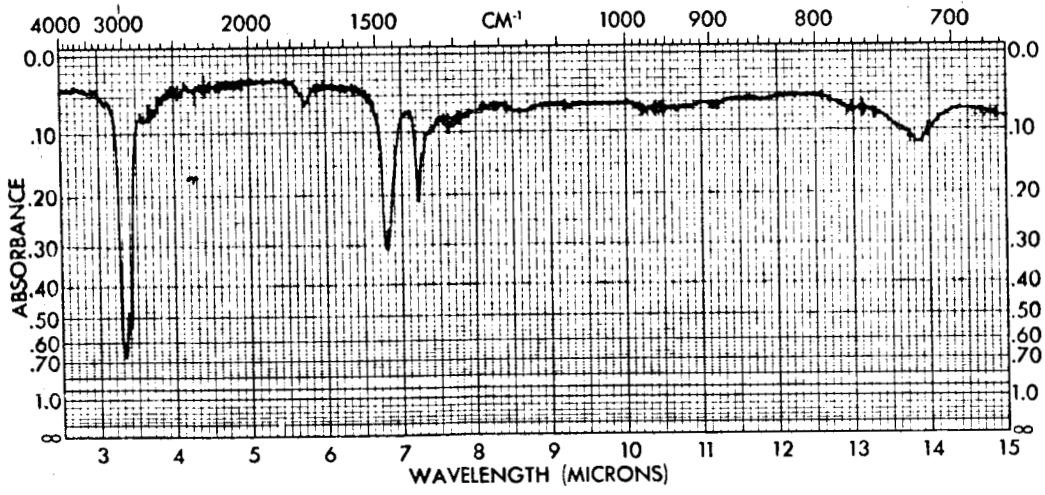
Hydrazinium nitrate was prepared from ammonium nitrate and hydrazine. The spectrum shown in Trace #1, Figure 17 was obtained placing this material between two sodium chloride windows under slight pressure. The spectrum shown in Trace #2, Figure 2 is that of a product spectrum obtained at -26°C in another of the low temperature runs, which was continued to this higher temperature.

The comparison of the two spectra leaves little doubt that the product of this reaction is hydrazinium nitrate. The melting point data (reported above) gives further support to this conclusion.

From the accumulated infrared data it is concluded that the low temperature reaction between N_2O_4 and N_2H_4 forms an intermediate adduct,

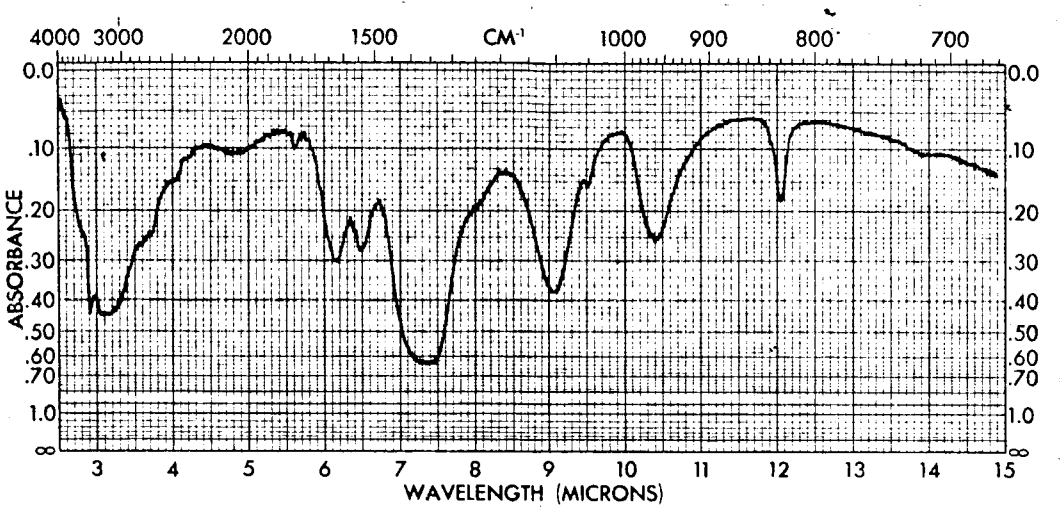


TRACE 1. AMMONIUM NITRATE (NUJOL MULL)

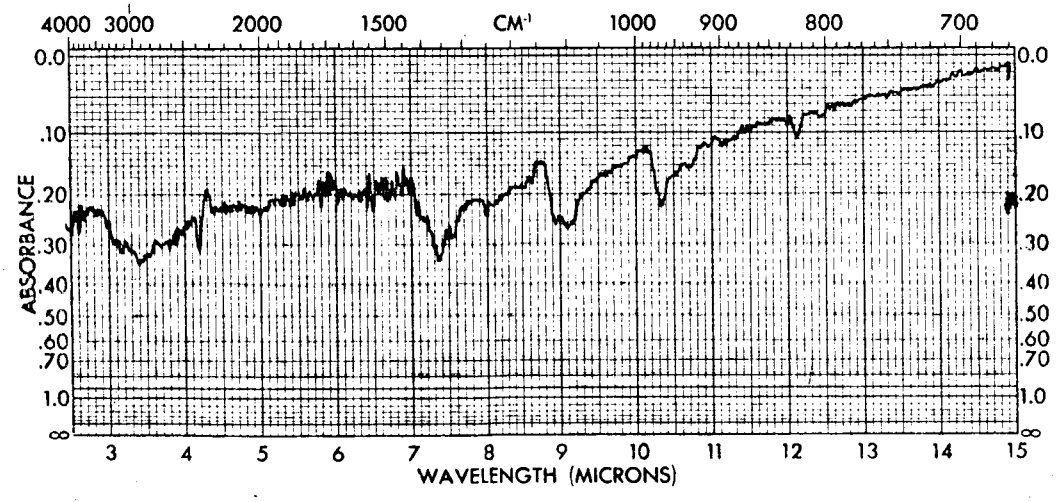


TRACE 2. NUJOL

FIGURE 16. INFRARED SPECTRUM OF AMMONIUM NITRATE



TRACE 1. HYDRAZINIUM NITRATE



TRACE 2. PRODUCT OF $N_2O_4 - N_2H_4$ REACTION (-26° C)

FIGURE 17. COMPARISON OF HYDRAZINIUM NITRATE SPECTRUM WITH PRODUCT SPECTRUM

which in turn reacts at about -50°C to form an intermediate capable of reverting to hydrazinium nitrate, nitrous oxide and traces of nitric oxide and nitrogen. To balance an equation in which N_2O and hydrazinium nitrate are formed from N_2O_4 and N_2H_4 requires ammonia as another reaction product, viz:

$$N_2O_4 + 2N_2H_4 \longrightarrow N_2H_5NO_3 + N_2O + NH_3$$

Curiously, ammonia has never been observed as a product in any of the reactions. An unidentified material having a vapor pressure of about 42.5 mm @ -111.8°C was observed, however. This material appeared on the gas chromatogram after N_2O (retention time 18 minutes).

B. HEAT OF REACTION

Experiments on this phase of the program were aimed at determining the heat liberated on initial contact between the propellant materials. Therefore, measurements were made of the heat liberated from the first reaction occurring as the mixtures were warmed from liquid nitrogen temperature.

A number of D.T.A. experiments were conducted using the apparatus shown in Figure 8. The results of two of these experiments are given in Figures 18 and 19. In the lower curve the potentiometer reading, obtained from the differential thermocouple located on the sample bulb and reference bulb, is plotted against time. The curves so obtained are above zero when the sample bulb is at a higher temperature than the reference bulb. The upper curves in these figures show the temperature of the reactor with time. This was obtained from a standard thermocouple attached to the bulb

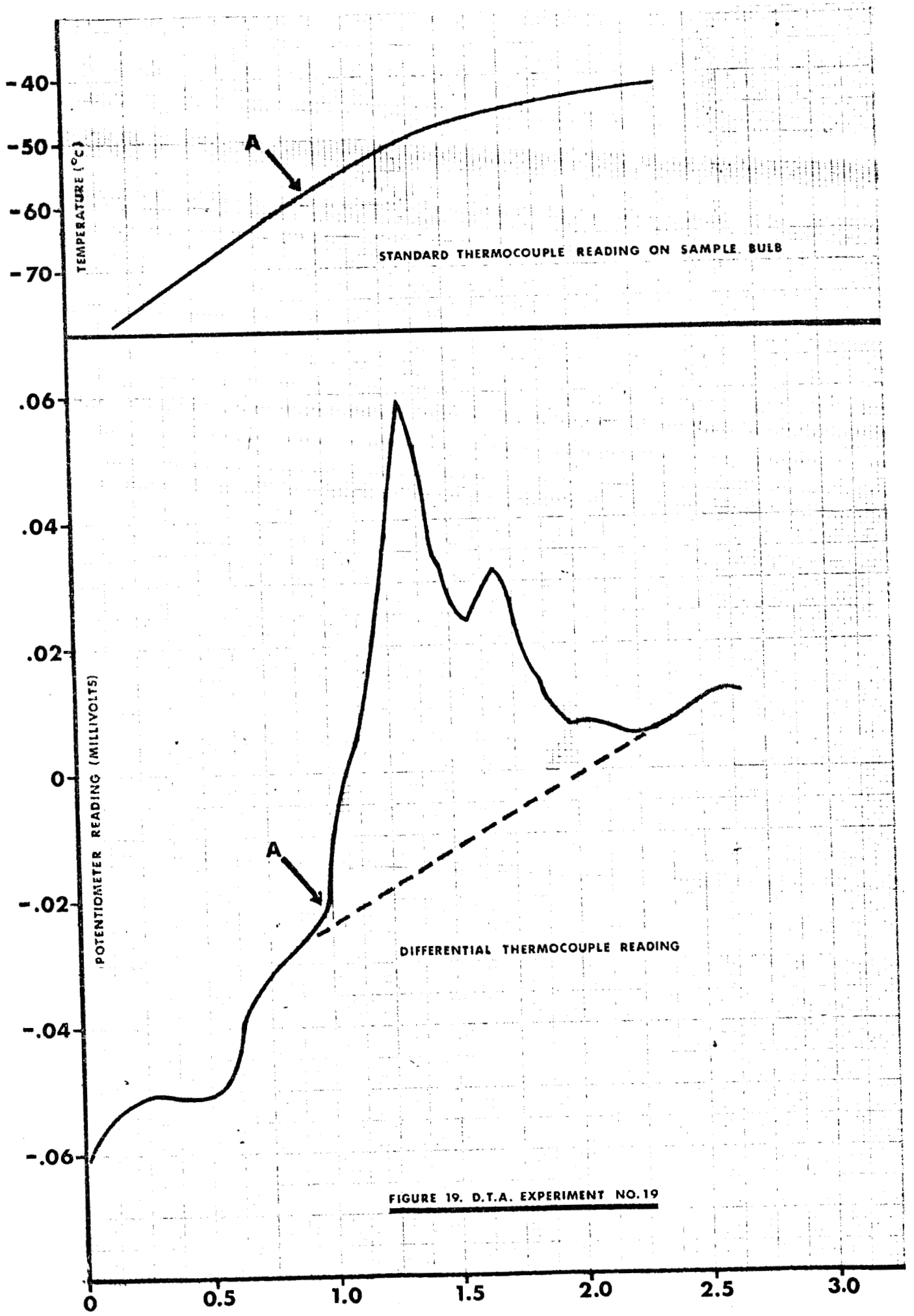


FIGURE 19. D.T.A. EXPERIMENT NO. 19

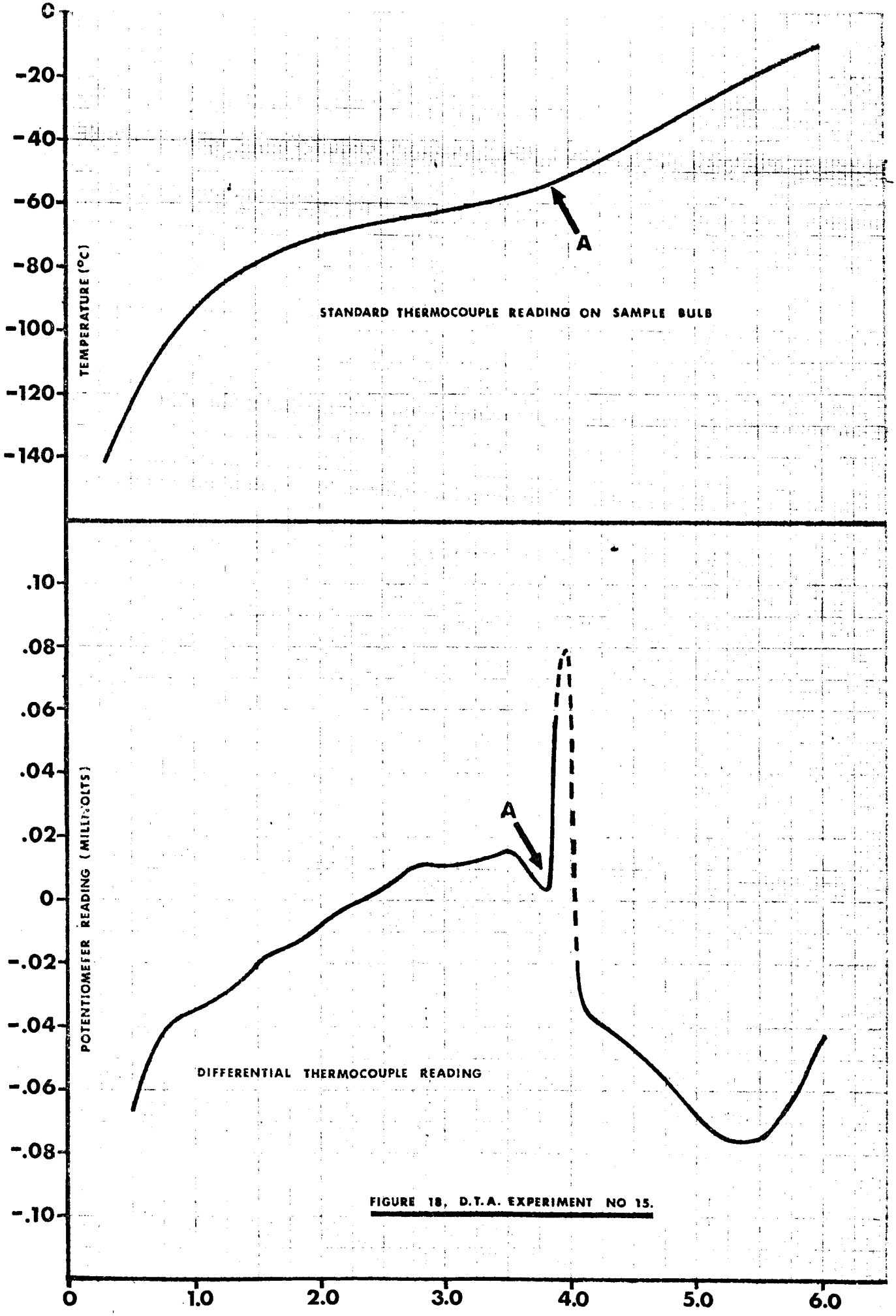


FIGURE 18, D.T.A. EXPERIMENT NO 15.

containing the N_2H_4-N_2O_4 mixture. By alternating readings it was possible to obtain both temperature and differential curves during the same run.

Experiment No. 15, one of the first D.T.A. experiments, is plotted in Figure 18. The variation in base-line in this curve is due to uneven warming of the sample and reference bulbs. Although the variation appears large, the temperature differences are actually small. For example, the difference for a copper constantan thermocouple is about 0.03 millivolts per degree in the temperature range -140° to $-20^{\circ}C$. Better control of the heating rate was obtained in subsequent experiments.

The start of an exothermic reaction is indicated as point (A) in the lower curve of Figure 18. It was impossible to keep up with the readings because of the rapid rate of change, and this portion of the curve is therefore shown as a dashed line. Projection of point (A) from the lower curve to the upper curve in Figure 18 shows that the exothermic reaction began at a temperature of $-54^{\circ}C$.

In another experiment, shown in Figure 19, the point of inflection of the D.T.A. curve (point A) occurred at a temperature of $-58^{\circ}C$. The broad base on this curve and the small rise occurring on the trailing edge of the main peak are attributed either to nonuniform reaction, or poor heat transfer to the thermocouple junction. Using the initial temperature rise as a measure of the energy release, a value of about one kilocalorie is calculated assuming reaction of all of the N_2O_4 (0.63 millimoles N_2H_4, 0.21 millimoles N_2O_4 present in reactor). It is impossible to know how much reaction had occurred in this experiment, and hence the calculated heat values

could be questioned. It should be noted, however, that the infrared traces indicate that all N_2O_4 and N_2H_4 has been consumed by the time the temperature has reached $-75^{\circ}C$.

No evidence of exothermic reaction was obtained at temperatures below $-58^{\circ}C$. These results are in agreement with the infrared studies if the initial low temperature reactions are assumed to be adduct formation, where relatively small energy change is involved. The lower temperature regions were those of least sensitivity in the D.T.A. apparatus, because the rate of increase of temperature was initially relatively large. The reaction at $-58^{\circ}C$ corresponds to the reaction in which N_2O was found by gas analysis.

The fact that reaction occurs at such a low temperature would suggest that rates of reaction at room temperature or above are extremely rapid. Assuming that these initial reactions are rate controlling, the N_2O_4-N_2H_4 reaction could be assumed to go to completion at all points of liquid contact in an engine.

Thus, the heat liberated at the point of contact between the two propellants is essentially that of the overall reaction:

$$N_2O_4 + 2N_2H_4 \longrightarrow 3N_2 + 4H_2O$$

or approximately 2 Kcal/mole of propellant mixture at the stoichiometric ratio.

C. MISCIBILITY

The dropwise addition of N_2O_4 to N_2H_4 was photographed, and visual comparisons were made between runs in which only pure N_2O_4 and N_2H_4 were present, and runs in which additives were present in either N_2O_4 or N_2H_4 or both. It was thought that either an increase in miscibility between the two propellants, or a substantial decrease in the rate of initial reaction between them might be beneficial in solving the problem of stream divergence. Visual observation appeared to be the quickest method for study of these phenomenon.

Initial tests were conducted with pure N_2O_4 being added to hydrazine containing 16% water. This test was chosen because this propellant system had given improved performance in JPL tests using a specified injector design. These photographs did not indicate increased miscibility, but showed instead an apparent decrease in the rate of reaction between the two propellants. No evidence was obtained of increased miscibility between the two reactants for any of the additives tried. However, apparent differences in reactivity were observed.

Although only qualitative estimates could be made of the relative reaction rates, it appeared that four types of reactions were occurring. These are shown in Table IV. All of the additives in the hydrazine appeared to decrease the rate of the initial reaction. The addition of iodine to N_2O_4, however, resulted in rapid ignition. The most dramatic change in reaction rate appeared when iodine was added to the N_2O_4 and a mixture of 1% Oronite NI-O and 16% water were added to the hydrazine. In this case the two liquids were actually in contact and did not tend to blow apart.

Table IV. Effect of Additives on N_2O_4 - N_2H_4 Reaction

	Additive in N_2O_4	Additive in Hydrazine % by Weight	Type of Reaction
1.	None	None	A
2.	None	16% H_2O	B
3.	None	16% H_2O KOH	B
4.	None	1% Santomerse	C
5.	None	1% Alkaterge A	C
6.	None	1% FC-126	C
7.	None	Oronite NI-O	C
8.	None	Oronite NI-W	C(1)
9.	1% I_2	None	-(2)
10.	16% H_2O	1% Oronite NI-O	C
11.	1% I_2	1% Oronite NI-O 16% H_2O	D

(1) Possible increase in solubility

(2) Ignited

Definition of Reaction Types

Type A: Rapid reaction which vaporizes N_2O_4 at surface of contact and causes N_2O_4 drop to be thrown out of the chamber.

Type B: Similar to A, except that reaction time appears slower.

Type C: Slow reaction time, and evidence of more extensive reaction between N_2O_4 and hydrazine resulting in violent interaction.

Type D: Reactants are in contact, reaction is mild with relatively slow "boiling" of N_2O_4.

Two additional runs on this system confirmed the slow rate observed in the first run. Therefore, a series of runs were made in which iodine was present in the N_2O_4 and the hydrazine additive was changed. The results are given in Table V. Of these runs, best results were still obtained with the Oronite-water additive to hydrazine.

Since the reaction between N_2O_4, containing iodine, and N_2H_4, containing Oronite detergents and 16% water, was noted to be significantly slower than the reaction without additives, additional photographs were taken in the hope that a system containing a smaller quantity of water, yet providing equally good results, could be found. The following sets were run and compared with previous runs containing 16% water:

Run No.	Additive in N_2O_4	Additive in N_2H_4*
1	Iodine (1%)	Oronite NI-O (1%) + H_2O (2%)
2	Iodine (1%)	Oronite NI-W (1%) + H_2O (2%)
3	Iodine (1%)	Santomerse-85 (1%) + H_2O (2%)
4	Iodine (1%)	Oronite NI-O (1%)
5	Iodine (1%)	Oronite NI-W (1%)

*The hydrazine used in these experiments gave the following analysis: Water 1.28%, Ammonia 0.03%, Aniline 0.54% (all percents by weight)

Of the above runs, only Run No. 4 was completely unsatisfactory, since this system ignited. Runs No. 3 and 5 appeared to be faster than Runs No. 1 or 2. Runs No. 1 and 2 were very similar, but on careful examination, Run No. 2 appeared the slower of the two.

The presence of iodine in the N_2O_4-N_2H_4 system was predicted to decrease the reaction rate between the two reactants since the reaction was thought to proceed by a free-radical mechanism. Surprisingly, the ignition delay time was shortened when iodine was added to the N_2O_4, and in the droplet experiment very rapid reaction and ignition occurred. When 16% water along with an Oronite detergent was added to the hydrazine the effect of iodine in the N_2O_4 could be noted. The experiments which were described above showed that the amount of water could be reduced to 2%.

The data obtained in these experiments was qualitative and no measure such as depth of penetration of N_2O_4, time to expel N_2O_4 from the hydrazine, etc. seemed adaptable to quantitative interpretation. A true test of the effectiveness of the tested additives could be obtained from engine tests. On the basis of the experimental program it was recommended to the Jet Propulsion Laboratory that engine tests be performed on the following systems:

Test No.	Additive to N_2O_4	Additive to N_2H_4
1	1% I_2	1% Oronite NI-W, 2% H_2O
2	1% I_2	1% Oronite NI-O, 2% H_2O
3	1% I_2	(None)

It was felt that these tests would cover the extremes of the slowest and fastest reactions obtained from these propellants with the tested additives. Thus, an increase in performance for any of these tests would give direction to additional additive studies.

Table V. Comparison of Relative Reaction Rates for N_2O_4-Iodine Samples

	Additive in N_2O_4	Additive in Hydrazine	Estimate of Relative Reaction Rates
1.	1% I_2	1% Oronite NI-O 16% H_2O	Slow
2.	1% I_2	1% Oronite NI-W 16% H_2O	Slow
3.	1% I_2	16% H_2O	Slow-Intermediate
4.	1% I_2	1% NI-W	Intermediate
5.	1% I_2	1% NI-O	Fast (Ignited)

IV. CONCLUSIONS

The data obtained in the work reported here is consistent with the fact that hydrazine-nitrogen tetroxide impinging jets are diverted by interactions between the two propellants. The principal factors which cause this phenomenon are:

(1) Immiscibility of the two reactants

(2) Rapid reaction rate between N_2O_4 and N_2H_4

(3) The high heat evolution and large gas volume generated by reaction

These factors are discussed in detail below:

A. IMMISCIBILITY

Although all three of the factors affecting stream divergence are closely related, it appears that miscibility is a major factor. Photographic studies showing the dropwise addition of N_2O_4 to hydrazine indicate the two materials to be completely immiscible. None of the pictures, with or without additives gave any indication of even partial miscibility of the two compounds. It is doubtful, therefore, that even with impinging jets, where the force of the two streams would tend to enhance mixing, that homogeneous mixing of the two materials could be effected.

Additives to promote miscibility still cannot be ruled out as possible solutions to this problem. However, mixing processes are generally considered to be relatively slow, even with miscible materials, and even improved miscibility may not overcome the rapid rate of reaction at the liquid-liquid interface.

B. REACTION RATE

It is reported here, that reaction between nitrogen tetroxide and hydrazine can occur at a temperature as low as -133°C. From measurement of the gas evolved at this temperature it appears that this initial reaction involves adduct formation between N_2O_4 and N_2H_4. The fact that no measurable heat is evolved in this initial reaction tends to support this view. A further reaction, involving heat evolution, occurs at about -58°C. These reactions were carried out under conditions where the rate of temperature rise could be carefully controlled. Thus, heat generated by the reaction was quickly dissipated and intermediates such as hydrazinium nitrate were capable of being isolated.

Under actual conditions in an engine, these initial reactions would occur very rapidly. This can be deduced from the "rule of thumb" that reaction rates double for every ten degrees rise in temperature. Not only would the initial reactions occur rapidly, but the heat evolved in these reactions would effectively increase the reaction temperature. On this basis, it is estimated that the reaction between hydrazine and nitrogen tetroxide would go to completion on contact, even in the very short contact time available in an engine.

C. HEAT AND GAS EVOLUTION

The stoichiometric reaction between these two propellants is given as:

$$N_2O_4 + 2N_2H_4 \longrightarrow 3N_2 + 4H_2O$$

It is this reaction that likely occurs at the contact surface of N_2O_4 and N_2H_4. The heat evolved from this reaction is of the order of 2 Kcal/mole of propellant mixture. This heat is available for expanding the large volume of product gases, or for vaporizing the propellants. It is not surprising, therefore, that the bulk of the liquid can be diverted by relatively small surface interaction.

It is difficult to conceive of a chemical approach which would solve this problem. It does not appear possible to prevent adduct formation or decomposition by the use of additives. It is possible that the rate of decomposition of intermediates such as hydrazinium nitrate could be altered chemically.

The most promising method of improving performance is injector design. It is important that the surface to volume ratio be as large as possible, so that essentially all of the liquid is contacted, thus minimum diameter jets or sheets of liquid appear optimum for this system.

V. REFERENCES

1. Johnson, B. H. "An Experimental Investigation of the Effect of Combustion on the Mixing of Highly Reactive Liquid Propellants," Technical Report No. 32-689, Jet Propulsion Laboratory, Pasadena, California (to be published)

2. Weiss, H. G., B. Johnson, H. D. Fisher and M. Gerstein. "Modification of the Hydrazine-Nitrogen Tetroxide Ignition Delay," AIAA Journal, pp. 2222-30 (December 1964)

3. Johnson, B. H. "Injector Development," Space Programs Summary No. 37-29, IV, pp. 100-102 (October 31, 1964)

4. Weiss, H. G. and E. B. Klusmann. J. Am. Chem. Soc., 84, 4993 (1962)