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THE CONSTANT PRESSURE DECOMPOSITION OF NITROUS OXIDE, N<sub>2</sub>O + .88N<sub>2</sub> AND N<sub>2</sub>O + AIR MIXTURES AT 11.2 ATMOSPHERES AND INITIAL TEMPERATURES FROM 772 TO 1233°K

54 p \$ 3.00 hc \$ 0.50 mg

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### FOREWORD

This interim technical documentary report was prepared by J. R. Nicholson, E. S. Fishburne and R. Edse of the Department of Aeronautical and Astronautical Engineering of The Ohio State University on Contract Number AF 33(657)-8951, Project 7065, Aerospace Simulation Techniques Research, Task 7065-01, Fluid Dynamics Facilities Research. The research on this task was administered under the direction of the Aerospace Research Laboratories, Office of Aerospace Research, United States Air Force, with Mr. John Goresh, Fluid Dynamics Facilities Laboratory, as Contract Monitor.

### ABSTRACT

The thermal decomposition of  $N_2O$ ,  $N_2O + .88N_2$ , and  $N_2O + AIR$  has been investigated in a flowing system. These studies were conducted at 11.2 atmospheres over the temperature range from 772°K to 1233°K, and total flow rates from 1.0 to 3.76 liters/sec. Total residence times in the heated section range from approximately .1 to 2.5 sec. A maximum reacted gas temperature of 1588°K was obtained. Chromatographic analysis of the products of decomposition showed that the maximum nitrogen dioxide yield was 4.44% for the  $N_2O$  + AIR mixture, 5.09% for the  $N_2O$  + .88N<sub>2</sub>, mixture, 7.55% for the pure  $N_2O$  decomposition. Spectrographic observations of the emitted radiation from the decomposition reactions showed the presence of nitrogen dioxide in the reaction. Nitrogen dioxide absorption bands were found. There was no evidence of any discrete bands in emission.

A reaction rate constant of 4.15 x  $10^{10} \exp \left\{-\frac{51,000}{R}\right\}$  was calculated

for the decomposition of nitrous oxide in the N20 + .88N2 mixture.

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LIST OF SYMBOLS

a	Indicates after the reaction	
A	Heater cross-sectional area	(cm <sup>2</sup> )
ъ	Indicates before the reaction	
c	Frequency factor	(sec <sup>-1</sup> )
Ea	Activation energy	(cals/mole)
h	Planck's constant - $6.623 \times 10^{-27}$	(gm cm <sup>2</sup> )
k	First order reaction rate	(sec <sup>-1</sup> )
Ko	Equilibrium constant for $\frac{1}{2}$ $0_2 \rightarrow 0$ reaction	$(atm^{1/2})$
L	Length of the heater	(cm)
ń	Mass flow rate	(gm/sec)
n	Specific molality	(moles/gm)
P	Pressure	(atm)
Po, Po2	Partial pressure of atomic and molecular oxygen	(atm)
R	Universal gas constant - 1.986	$\left(\frac{\text{cal}}{(\text{mole}) (^{\circ}\text{K})}\right)$
	82.06	$\left(\frac{(\text{atm}) \ (\text{cm}^3)}{(\text{mole}) \ (^{\circ}\text{K})}\right)$
T	Gas temperature	(°K)
Ŧ	Average gas temperature in heater	(°K)
ប	Average linear gas velocity through heater	(cm/sec)
∆H <sup>O</sup>	Standard heat of formation at O <sup>O</sup> K	(cal/mole)
AHT	Heat of formation at indicated temperature	(cal/mole)
m	Molecular weight of the mixture	(gms/mole)
ni	Mole fraction	

### LIST OF SYMBOLS (CONT'D)

ē	Average gas density	$(gms/cm^3)$
<b>Y</b> R	Residence time of the gas in the heater	(sec)
v	Frequency of emitted radiation	(sec <sup>-1</sup> )
v	Standard volume flow rate	(liters/sec)
(N2Q)	Concentration	(moles/cc)
*,**	Excited states	

3\*, 3\*\* 32 or 3x states

### SECTION I

### INTRODUCTION

The advent of hypersonic flight and re-entry flight into the earth's atmosphere has introduced experimental difficulties in adequate simulation of the aerodynamic characteristics for these conditions. Current materials technology has limited the maximum stagnation temperature to which air can be heated by conventional methods on a steady state basis to approximately 2000°K. Transient tests with zirconia pebble bed heat exchangers have been conducted with stagnation temperatures to approximately 2500°K; however, it is desirable to establish steady state conditions for extended periods of time so that more reliable measurements in the test cabin can be made. For the complete simulation of hypersonic flow characteristics, stagnation temperatures and pressures must be sufficiently high to permit not only Mach number simulation but also adequate Reynolds number simulation. Due to the high expansion ratio of the high Mach number nozzles, the static temperature of the exit gas is quite low, and in some cases, the gas (i.e., nitrogen and oxygen) may liquify. Obviously this phenomenon prevents us from achieving homogeneous flow.

The primary interest for the use of nitrous oxide as a wind tunnel testing medium results from the fact that the heat of reaction from the decomposition of nitrous oxide is approximately 20,000 cal/mole, assuming complete decomposition. Based on the results presented in Ref. 1 through 3, it appears that a completely self-sustaining decomposition of nitrous oxide is practical and possible. The resulting products of decomposition of nitrous oxide are 66% nitrogen and 33% oxygen for the complete decomposition. The adiabatic temperature rise for the pure nitrous oxide decomposition based on theoretical calculations (Appendix I) is approximately 1600°K. Assuming a preheat temperature of 1200°K, final gas temperatures of 2800°K are possible. Current state-of-the-art techniques allow heating pure nitrogen to a temperature of approximately 3000°K with graphite heaters. The temperature of the resulting mixture will be approximately 2900°K. This permits the attainment of steady state stagnation temperatures considerably higher than the highest currently being employed in the simulation of hypersonic conditions. For the complete decomposition reaction, N20 + .88N<sub>2</sub>, the products are 1.88 N<sub>2</sub> + .50 O<sub>2</sub>. This composition duplicates that of air.

The decomposition reaction of nitrous oxide has been investigated rather extensively by constant volume bomb methods; however, this does not provide adequate information for a flowing system or a constant pressure decomposition. The fundamental purpose in the design of this system was to permit the investigation of the decomposition reaction of nitrous oxide for constant pressure conditions. It is necessary, therefore, to determine the conditions which lead to complete decomposition of nitrous oxide, the species concentration and maximum achievable temperatures. The constant pressure decomposition of nitrous oxide has been investigated (Refs. 1-3, 12). Investigation of the constant volume decomposition of nitrous oxide has been conducted by various investigators (Refs. 4 through 12). In general, the primary interest has been in the ures of the constant volume reaction. Investigations into the processes of decomposition during the constant pressure process at elevated pressures has not been investigated in detail. It is also of interest to determine the temperature of the reaction and the effects of the heating medium and the vall surfaces. It has been determined by other investigators (Refs. 1, 9-11) that nitric oxide is a fundamental product of the decomposition reaction. Since this occurs as a product of one of the steps of the reaction, it is most probable that any system using nitrous oxide must accept the existence of the nitric oxide; however, it would be expected that certain experimental techniques could be utilized to minimize the formation of nitric oxide.

Various methods of initiating the decomposition reaction were considered. Among these were electrothermal heat addition, electric arc energy addition, or by the addition of a nitrous oxide stream (heated to just below the decomposition temperature) to a high temperature stream of nitrogen. It was decided that the appropriate approach to this experimental program was to obtain the results from direct electrothermal heat addition to the nitrous oxide. The effects of various additives to the gas are considered (i.e., nitrogen and air). The latter approach considered will be the approach taken in a future investigation at this Laboratory.

### SECTION II

### EXPERIMENTAL APPARATUS

The experimental apparatus utilized in this investigation was discussed in detail in Ref. 8. A brief discussion of the apparatus will be included.

The reaction vessel is illustrated in Fig. 1. This vessel is made of stainless steel pipe, 8-1/2" I. D. x 1-1/8" wall thickness, 10 feet long. It was designed to withstand a maximum working pressure of up to 200 atm. The flanges on each end provide ready excess to the internal heaters in the reaction chamber section.

The heaters are constructed of 1" I. D. alumina tube with a 1/8" wall. The tubes are wrapped with approximately 90 turns of .040" Kanthal A-1 resistance wire. The maximum operating temperature of this heater is approximately  $1600^{\circ}$ K. A coating of alumina cement was placed on the outer surface of the tube to provide structural support to the resistance wire and to increase the heat transfer coefficient from the wire to the tube. Each of the four sections of the heater have a power dissipation of 3 kilowatts at 220 volts AC. It was found that

this power input was completely adequate and in most cases created thermal overshoot problems. A rather serious disadvantage to this heater design was the small wire size. The lifetime of the smaller diameter wire is reduced considerably. A more appropriate design would have utilized large diameter wire, with a low-voltage, high-current power supply.

Heater temperature control was obtained with four Simplytrol thermocouple actuated temperature controllers. The schematic diagram is shown in Fig. 2. The chromel/alumel thermocouples for control of the wall temperatures were imbedded in the outer surface of the ceramic cement coating at the downstream and of the heater. The percentage on-time of the heaters is controlled by means of conventional percentage timers. This permitted control of the average rate of power input into the system at a constant supply of voltage, helping to eliminate the effects of thermal overshoot.

A similar arrangement was utilized for the reaction section. There are a total of 5 sections in the reaction zone. The original concept was that the first four sections which are heated sections would act as a preheater, and the reaction would occur in the first five sections of the reaction zone. Due to the extremely rapid reaction, it was impossible to shift the reaction from the heater into the reaction zone. This problem will be discussed in further detail in Section III.

In the original design of the system, a fixed orifice for exhausting the gases to the atmosphere was used. It was found, however, that due to the combined effects of increased temperature and volume flow rate caused by the decomposition, the pressure level could not be adequately controlled to maintain a constant internal pressure. A variable pressure switch was used in conjunction with a solenoid valve to pressurize or depressurize a pneumatically operated Annin valve. This arrangement worked quite well and maintained the pressure in the reaction vessel to within  $\pm 2$  psig of the desired operating pressure.

An observation window with a 1" diameter opening is located on the upstream flange. This provides visual observation of the reaction and the heaters. It was originally anticipated that optical pyrometer temperature measurements of the probe might be made; however, due to the luminosity of the reaction, it was impossible to observe the probe. For normal experiments, a window made of Herculite glass, 1-1/4" thick, was utilized; however, during some of the spectrographic measurements, a quartz window was used to eliminate the absorption effects in the short wave length regions.

A water-cooled probe is used to obtain gas temperatures and gas samples. This probe can be moved axially throughout the entire length of the reaction chamber and heater assembly. The positioning arrangement and locking mechanism for the probe is illustrated in Fig. 1. The gases removed for sampling are quenched by the internal water cooling. Since the water temperature at no time exceeded 120°F, the quenching effect was quite adequate. Original design of the thermocouple probe incorporated a tungsten/tungsten-26% rhenium thermocouple for temperature measurements above 2000°K. Since the observed temperatures were well within the temperature range of chromel/alumel thermocouples, a sheathed chromel/ alumel thermocouple was used in place of the tungsten/tungsten-26% rhenium thermocouple. Better measurement accuracy was obtained in the lower temperature region observed.

Gas samples are withdrawn from the reaction tube into evacuated 250 ml Pyrex flasks. These flasks are connected to the vacuum pump until the sample is obtained. A three-way solenoid valve is used to divert the sampling stream from a vent into the sampling flasks. The flasks are then flushed approximately 15 to 25 seconds for a total volume change of approximately 10 to 15 times. This virtually eliminates the presence of impurities in the sample. These flasks are evacuated to an absolute pressure of approximately 100 microns before the samples are taken.

An F and M Scientific Corporation Model 500 Linear Temperature Programmed Gas Chromatograph is used to analyze the gas samples. A molecular sieve 5A column, 42 inches long is used. Various methods of determining the composition of mixtures of nitrogen, oxygen and the oxides of nitrogen (i.e., nitric oxide, nitrogen dioxide and nitrous oxide) are given in Ref. 13 through 16. Since the mixture of the oxides of nitrogen in the presence of oxygen is very reactive at room temperature, this makes the complete analysis of these gases extremely difficult by gas chromatography. However, when analyzing mixtures containing nitrogen, oxygen, nitrogen dioxide and nitrous oxide, it was observed that there were 4 distinct indications of the various constituents. Comparisons with mixtures of nitrogen, oxygen, nitrous oxide showed that three of the peaks could definitely be identified as produced by these constituents. The fourth peak was considered to be that corresponding to the composite of the equilibrium mixture of the oxides of nitrogen at room temperature. In an attempt to obtain a direct calibration for the percentage of the oxides of nitrogen, equilibrium mixtures of nitric oxide and air were made. At room temperature nitric oxide in the presence of a large excess of oxygen reacts nearly completely to form an equilibrium mixture of nitrogen dioxide and nitrogen tetroxide. Equilibrium constants for the reaction

### 2 NO2 2 N204

were obtained from Ref. 17. At room temperature  $(20^{\circ}C)$  and a very small concentration of nitrogen dioxide, this reaction is almost completely shifted to the left side. According to the Le Chatelier principle, high pressures will shift the reaction to the right. Increasing temperatures will shift the reaction to the left. For total percentages of the oxides of nitrogen less than 5%, the reaction is shifted approximately 95% to the left.

Calibration of the detector response to various percentages of the oxides of nitrogen were performed to determine if the total percentage could be determined directly. Quite interestingly enough, the height of the composite peak was linearly related to the number of moles of the equilibrium mixture of the oxides of nitrogen and air; however, at very low concentrations, the slope of the calibration curve shifted quite drastically. The sensitivity of the detector to extremely small amounts of the oxides of nitrogen at very low partial pressures was much higher then for higher percentages. This was corroborated by observations of the analyses of the mixtures of nitrous oxide which had obviously not decomposed. In some cases where there was approximately 1/2% of oxygen present in the sample, a slight peak was observed before the nitrous oxide peak. Since the equilibrium constant at room temperature for the reaction

$$NO + 1/2 O_2 = NO_2$$

is approximately 10<sup>6</sup>, effectively all of the nitric oxide will be oxidized to nitrogen dioxide in the presence of excess oxygen.

Visual observation of these sample flasks showed that the presence of nitrogen dioxide must be less than .01% since no brown color could be detected. It is felt, therefore, that if nitric oxide is formed in the reaction, its concentration was less than .01%. Calibration for the other constituents in the gas (i.e., nitrogen, oxygen and nitrous oxide) was performed with dry high pressure air and a calibration gas which consisted of nearly equal parts of oxygen, nitrogen, and nitrous oxide. In Ref. 8, a method of determining the amount of nitrogen dioxide in the sample was outlined. This method required dry ice-alcohol traps to freeze out the nitrogen dioxide, and analyze the mixture by difference. It was found by subsequent analyses, that the small percentage of nitrogen dioxide in the mixture (i.e., from 1% to 5%) lead to rather serious errors in the determination of this percentage. The analysis for the mixture of the oxides of nitrogen was conducted as described above. In addition, the nitrous oxide percentage was determined directly. The total percentage of nitrogen plus oxygen was then determined by difference, and the individual percentages of nitrogen and oxygen were determined by area ratios. The appropriate correction for thermal conductivity differences between the two gases was applied to the area ratio.

The spectrographic techniques utilized in the study involved four basic pieces of equipment. Initial observations were made with a small Bausch and Lomb hand spectroscope. Those observations clearly revealed the presence of various band systems. For a more refined spectral analysis a Hilger-Watts quartz prism spectrograph was used. This instrument utilized 3-1/4" x 4-1/4" glass plates. It was found, however, that due to the characteristics of the quartz prism and the fact that the spectral regions of primary interest was above 4500 Å, the dispersion of the quartz prism was insufficient to permit any adequate interpretation of the spectra. Subsequently, a Bausch and Lomb Medium Cornu Spectrograph was used. This instrument was used primarily to determine the existence of the continuum cut-off point. Greater resolution was obtained with a Jarrell-Ash 21-foot Grating Spectrograph. Various films and plates were used. Eastman Kodak Tri-X, Type I-N, and I-O Spectroscopic 35mm films were used. Type I-N, II-F, and IV-O 4" x 10" glass plates were also used. The geometric arrangement of the light path is shown in Fig. 3.

### SECTION III

### EXPERIMENTAL RESULTS

### (1) Pure N20 Decomposition

The decomposition reaction of pure nitrous oxide was investigated at a pressure level of 11.2 atmosphere. Flow rates of 1.0 to 2.0 liters per second were used. Initial temperature levels from 772°K to 1138°K were investigated. The results are tabulated in Tables I through III.

Initial experiments were conducted with an air purge to stabilize the temperature of the heaters. It was found, however, that the samples were taken before the nitrous oxide had completely eliminated the air from the test section. Subsequent experiments were conducted with pure nitrogen as the stabilizing medium. Air leaks into the reaction chamber were also observed. These leaks were apparently caused by an aspiration effect at the junctions of the heater sections. During the remainder of the experiment, the annular cooling air was terminated during the experiments to eliminate this problem.

The procedure followed during these experiments was to stabilize the heaters at some temperature level with pure nitrogen at a flow rate of approximately 1.0 liters/sec. After the temperature had stabilized, the nitrogen flow was terminated, and the nitrous oxide flow was started immediately. There was a rather long lag time (approximately 15 seconds) before any reaction was observed. This lag occurred at all temperature levels. Most likely this lag was caused by the long distance (approximately 35 feet) between the flow control panel and the reaction vessel, and the initially high concentration of nitrogen in the reaction chamber. Approximately 30 seconds after the nitrous oxide flow was started, the sample was taken. Approximately 15 to 25 seconds were needed to insure adequate flushing of the sample flask. Upon completion of sampling, the nitrous oxide flow was terminated and nitrogen was introduced.

During the experiments with pure nitrous oxide, some rather interesting results were noted. The luminosity from the reaction generally appeared to begin at the far end of the heater section, and then very rapidly traveled back to the area of the injectors and observation window. Visual observation of the color of the emitted radiation showed that there are apparently two distinctly different types of radiation. During the "initiation period", the time between the first indication of a reaction and the transition into a stable decomposition reaction, the color is a brilliant yellow. After the reaction is stabilized, the color is more reddish-orange. The results of the spectrographic studies will be discussed more completely in a later section.

Great difficulties in obtaining a partial decomposition of the nitrous oxide were experienced with all experiments with pure nitrous oxide. Associated with the "transition" phenomena discussed above, was the virtual impossibility of obtaining a partial decomposition. All samples taken showed that the nitrous oxide either did not decompose, or that the reaction had gone virtually to completion.

The measured temperature of the reacted gases was always much less than indicated by theoretical calculations. The adiabatic decomposition temperature rise for this reaction should be approximately 1600°K (Appendix I and Figure 4), assuming that there is no dissociation of the oxygen and that no intermediate compounds, such as nitric oxide and nitrogen dioxide, are formed. Existence of the latter constituents in the system will lower the calculated value of the temperature. Experimental results tabulated in Tables I-III show that the maximum observed temperature vas observed at the outlet of the first heater section, with a total flow rate of 2.0 liters/second.

The data on the results with the pure nitrous oxide system are somewhat scattered; however, the formation of nitrogen dioxide in this system increases with increasing initial temperature and with increasing flow rates.

Reference 10 presents a set of reactions as follows

$n_2 0 \rightarrow n_2 + 0$	(1) $\Delta H_0^0 = + 38.3$ kcal
$0 + N_2 0 \rightarrow N_2 + 0_2$	(2) $\Delta H_0^0 = -78.9$ kcal
$0 + N_2 0 \rightarrow 2 N 0$	(3) $\Delta H_{8}^{2} = -35.9$ kcal
$0 + N0 + M \rightarrow N0_2 + M$	(4) $\Delta E_0^0 = -71.4$ kcal
0 + 0 + Wall - 02 + Wall	(5)
$NO_2 + N_2O \rightarrow N_2 + O_2 + NO$	(6) $\Delta H_0^0 = -7.5$ kcal

where  $\Delta H_8^0$  = heat of formation at  $0^{\circ}K$ 

According to this set of reactions, it is difficult to explain the presence of the radiation. Kaufman, et al (Ref. 10), observed the radiation and ascribed it to the fluorescence of the electronically excited nitrogen dioxide molecule. Reuben and Linnett (Ref. 9) have postulated that the set of activation equations are

$$N_20 + N_20 \rightarrow N_20^* + N_20$$
 (1a)

 $N_20^* + N_20 \rightarrow N_20^{**} + N_20$  (1b)

$$N_2 O^* \rightarrow N_2 O^{3^*}$$
 (2a)

 $N_20^{*} + N_20 \longrightarrow N_203^{*} + N_20$  (3a)

$$N_20^{**} \rightarrow N_203^{*}$$
 (4a)

$$N_20^{++} + N_20 \rightarrow N_20^{3^+} + N_20$$
 (5a)

$$N_0 O^3 \rightarrow N_0 + O^4$$
 (6a)

$$N_2 O^{3**} \rightarrow N_2 + O^*$$
 (7a)

where  $3^{\#}$  and  $3^{\#\#}$  are the  $3\Sigma$  and  $3_{\pi}$  states, although not necessarily in that order, and the symbols # and ## are used to designate an excited state. Assuming that nitrous oxide decomposes according to reactions (1) through (6), and that the unimolecular decomposition reaction of nitrous oxide occurs as indicated in (1a) through (7a), reaction (1) will be modified to

No - No + 0\*

Assuming that excited atomic oxygen atoms are formed, equation (4) can be written as

$$0^{+}$$
 + NO + M  $\rightarrow$  NO<sub>2</sub><sup>+</sup> + M

The radiation would then originate from the excited nitrogen dioxide molecule

$$NO_2 \rightarrow NO_2 + hv$$

where h = Planck's constant

### v = Frequency of the emitted radiation

Based on the observed experimental results, it is expected that the rate of reaction (3) increases faster with increasing temperature than that of equation (2).

As determined by other investigators (Ref. 10), nitric oxide is formed during the early stage of the reaction and subsequently inhibits the formation of additional nitric oxide. These results are in agreement with the results obtained for increasing flow rate, i.e., larger amounts of nitrogen dioxide formed.

The existence of wall effects or a wall reaction is indicated by the observed reactions and maximum temperature increases observed. As would be expected, if the effects of a wall reaction are present, the temperature rise will decrease with increasing temperature, and will increase with increasing flow rate. An increasing wall temperature will cause the wall reaction to accelerate, thereby increasing the amount of heat transfer to the wall. Increasing flow rate will shift the reaction downstream, thereby causing more energy transfer to the gas stream. In addition, further verification of this effect is shown by the increasing temperature rises obtained as the probe is moved towards the inlet.

It was demonstrated that a self-sustaining reaction could very easily be maintained for the initial conditions and flow rates considered. This self-sustaining reaction was accomplished several times and it continued after all electrical energy had been cut-off; however, these experiments were not allowed to reach a stable state since the observed wall temperature rose to approximately 1300°K. This temperature is approaching the maximum safe usable limit of the heaters.

During the experiments in which the probe was positioned at the exit of the first and second heaters, observations of the reaction vessel showed that a reaction was occuring downstream of the probe. Since this occurred at temperatures lower than previously determined required for initiation of the reaction  $(859^{\circ}K)$ , it was expected that there might possibly be catalytic effects present. Sample probes of stainless steel, copper and silver solder covered stainless tubes were constructed. Interestingly, conditions which lead to no decomposition with stainless steel and copper tubes, produced a decomposition reaction when the rods were coated with silver solder. After causing a single decomposition, no further reactions could be initiated. Removal of the probe and repolishing the surface of the probe led to initiation of a reaction when re-inserted

The reactions on the surface of the probe most probably lead to the initiation of the reaction; however, the possibility of the probe acting as a "flame holder" may also play an important role in this effect. Corresponding to these effects is the low temperature required for initiation of the reaction when the probe was positioned at the outlet of the first heater. Characteristics of the vortex flow may also explain the low observed temperature required for initiation. Since the lengthdiameter ratio was from 12 to 24, a fully developed turbulent flow is probably not established. Large temperature gradients may exist in the gas stream under these conditions.

During visual observations of the reaction, it was noticed that a pulsation in the luminosity occurred. The frequency of the oscillation increased with increasing flow rate, and indeed, the luminous zone extended completely to the inner surface of the window. The presence of the

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radiation at the window is quite difficult to understand, since the gas temperature in this region is not higher than  $450 - 500^{\circ}$ K. This observation can possibly be explained by a catalytic effect. The origin of the pulsations is not clear.

To consider the factors leading to the pulsation, the characteristics of the flow must be analysed. The injectors are designed to create a vortex flow necessary to provide maximum heat transfer to the gas. One of the four injectors is bent so that direct impingement of the gas on the window is effected to eliminate a possible "pocket" of cold reacted gases. Due to the high tangential peripheral velocity, a stagnant region in the center of the tube will exist for a short distance downstream of the inlet. In this region, which is somewhat cooler than the gases at the periphery due to the lower heat transfer rate, the reaction will occur at a slower rate. Products of the reaction zone around the periphery of the tube surface vill be carried into the center of the tube, accelerating the reaction in the center. After completion of the reaction, the effect of the inert diluents (nitrogen and oxygen) in the center of the tube will be transported downstream, being continually replenished with fresh nitrous oxide. When the composition of the gases along the centerline of the tube becomes suitable, rapid reactions will again occur. This will then lead to a periodic reaction along the centerline of the tube.

(2) N<sub>2</sub>0 + .88N<sub>2</sub>

Experiments were conducted with mixtures of  $N_20 + .88N_2$ , in a similar manner as described previously for the pure nitrous oxide experiments. The results are presented in Tables IV through VI. The maximum amount of nitrogen dioxide found during this investigation was 5.09%, although, in general, the amount determined was somewhat less than found in the pure nitrous oxide experiments. A larger temperature rise was obtained with the N<sub>2</sub>0 + .88N<sub>2</sub> mixture for flow rates corresponding to the pure nitrous oxide decomposition. In addition, since the theoretical temperature rise for the N<sub>2</sub>0 + .88N<sub>2</sub> mixture is approximately 1000°K (compared to 1500°K for the pure nitrous oxide decomposition), the percentage of the theoretical temperature rise for the N<sub>2</sub>0 + .88N<sub>2</sub> mixture was always greater than that observed for the pure nitrous oxide reaction.

Difficulties in obtaining a stable partial decomposition reaction were also encountered with this mixture. With the exception of three cases, the reaction went nearly 100 per cent to completion. Evaluation of the partial reactions permitted the calculation of a reaction rate constant.

The calculation of the first-order reaction rate constant is given in Appendix II; the value obtained is

$$k = 4.15 \times 10^{10} \exp\left\{-\frac{51,000}{R}\right\}$$

The first-order reaction rate is of the form

 $k = c \exp \left\{-E_{a}/R_{T}\right\}$ 

where

c = frequency factor =  $4.15 \times 10^{10} \text{ sec}^{-1}$ E<sub>a</sub> = activation energy = 51,000 cal/mole T = initial temperature

This first-order reaction rate agrees rather well with the data obtained in Ref. 18. The activation energy is somewhat lower than values obtained by other investigators. This is probably due to the effects of the wall reactions. The frequency factor which was determined is also low. This is in agreement with the data obtained by many other investigators.

Visual observations of the reaction vessel showed that the radiation was nearly optically transparent, as compared to the pure nitrous oxide decomposition which was optically opaque. In addition, the color of the gas was much more yellow. These results can be explained by the decreased nitrogen dioxide formation.

(3)  $N_20 + AIR$ 

Results of the experiments with  $N_20$  + AIR are presented in Table VII. Total gas flow rates of 2.0 and 3.0 liters/sec were used, with the probe positioned at the outlet of the fourth heater. The maximum temperature rise for this particular position and flow rate is higher than that obtained either with the pure nitrous oxide or the  $N_20$  + .88N<sub>2</sub> reactions. It is therefore concluded that the reaction rates follow the following scheme:

 $k_{N_20} > k_{N_20} + .88N_2 > k_{N_20} + AIR$ 

At the maximum flow rate, and temperatures considered, no decomposition was obtained for this mixture.

Visually, the radiation from this reaction appeared to be similar to that obtained with  $N_2O$  + .88N<sub>2</sub> mixtures.

### (4) Spectrographic Observations

Initial investigations of the radiation from the decomposition reaction of pure nitrous oxide were made using a small hand spectroscope. The results of these investigations indicated that it would be worthwhile to attempt to identify the origin of the radiation. For this purpose, a rather elaborate optical path was constructed, shown in Fig. 3, to utilize the Jarrell-Ash 21-foot grating spectrograph. Since there appeared to be two distinctly different colors (i.e., bright yellow during the starting process and reddish-orange during stable decomposition) attempts were made to obtain the spectra of each phase. Figure 4 shows the spectra obtained with Eastman Kodak Tri-X film. Although the film sensitivity decreased quite rapidly for wavelengths longer than 6500 Å, in the region of primary interest (5500 Å), it was sufficient to obtain the spectrum.

The radiation during the starting process was photographed by repeated exposures. No bands in absorption were found in this phase of the reaction; however, the steady state reaction produced a band spectrum in absorption as shown in Fig. 4. In both cases, however, a continuum background was observed. The intensity of the continuum was apparently much greater for the case of the steady state reaction.

To identify the system observed, it was necessary to obtain a reference spectrum of possible constituents. A small absorption cell, with a path length of 1" was filled with either nitrous oxide, nitric oxide or nitric oxide plus excess air. Light from a tungsten filament blackbody source was passed through the cell. Virtually no absorption was observed with the nitric oxide and very slight absorption around 4000 Å was observed with the nitric oxide; however, the equilibrium mixture of nitric oxide plus excess air at approximately 100 psig resulted in a very complex absorption system. Comparison of the absorption spectra obtained from the reaction vessel with the reference spectra, indicated that the nitrogen dioxide molecule gave rise to the observed absorption spectra.

To obtain an absorption spectrum, the presence of a background source is necessary. Great care was taken to eliminate the blackbody radiation of the heater walls as a source of the continuum background. Repeated exposures for very short intervals (10 seconds), produced similar results to the longer exposures, i.e., identical absorption bands were observed with a continuum background. It is, therefore, concluded that the observed continuum was produced in the reaction rather than being caused by the blackbody radiation of the heaters.

A Bausch and Lomb Medium Cornu Spectrograph was positioned directly at the reaction vessel to determine if the apparent continuum had a cutoff at any particular wavelength. For cumulative exposure times of 90 seconds at 15 seconds per exposure, slit widths of 10, 50 and 200 microns, and type IV-0 spectroscopic plates, a continuum was observed down to approximately 3200 A; however, no discrete cut-off point was observed. A spectrogram of the stable decomposition reaction obtained by this spectrograph is shown in Fig. 5. Since the recombination continuum of the NO + 0 NO<sub>2</sub> reaction should cut-off at about 4000 Å, it is believed that this reaction is not the principle reason for the radiation. Kaufman, et al (Ref. 10) have postulated that the radiation is caused by chemiluminesence rather than thermal nitrogen dioxide molecule radiation. Since the nitrogen dioxide lines have been identified, the absorption bands are most probably due to self-absorption phenomena.

The mechanism of chemiluminesence of the NO + O recombination reaction was studied by Clyne and Thrush (Ref. 19). The absorption spectra of an equilibrium mixture of nitrogen dioxide and nitrogen tetroxide in the spectral region from 2400 to 5000 Å was determined by Hall and Blacet (Ref. 20). Fluorescence spectra of the nitrogen dioxide molecule were investigated in the region above 4000 Å by Neuberger and Duncan (Ref. 21) using Raman spectrum techniques. The results obtained by Ref. 20 and 21 are of considerable interest in confirmation of the observed spectra.

The absorption spectra of nitrogen dioxide has a maximum at approximately 4000 Å with decreasing absorptivity towards longer and shorter wavelengths. The spectra showed the presence of some fine structure. The intensity of the absorption decreases continually with decreasing wavelengths down to approximately 2500 Å, although the absorptivity at 4000 Å is approximately 45 times as great as at 2500 Å; on the other hand, the absorptivity at 4000 Å is approximately 2-1/2 times as great as at 5000 Å. Neuberger and Duncan (Ref. 21) indicate that an absorption spectrum against a continuum background was obtained for relatively low nitrogen dioxide pressures (approximately 12 microns).

The observed results are in agreement with Refs. 20 and 21. Since the observed continuum extended to approximately 3200 A, this may be caused by the radiation of the hot nitrogen dioxide molecule. Based on the absorption characteristics of nitrogen dioxide, similar emission characteristics due to thermal effects should be possible. The precise shape and position of the curve would probably be different due not only to different transition probabilities, but also due to the higher temperatures encountered in this investigation, 1000 - 1200°K, as compared to 300°K in Ref. 20. The higher vibration levels will be more highly populated due to the increased temperature level; thereby, shifting the maximum of the curve. The curve should also be flattened providing a more nearly constant emission spectra, over a broader spectral range.

This is, in fact, in agreement with the observed spectra. Since nitrogen tetroxide will be non-existent at the temperature levels obtained, no effect due to the short wavelength absorption will be encountered, and nitrogen dioxide will be the only source of the observed spectrum. It is somewhat questionable as to whether the total spectrum is only a function of the hot nitrogen dioxide radiation, or whether fluorencence may also account for some of the radiation in the region above 4000 A (Ref. 21).

### (5) Conclusions

The use of nitrous oxide as a working medium for a hypersonic wind tunnel requires a maximum total temperature rise (minimum heat loss) with a minimum formation of nitric oxide and nitrogen dioxide. Due to the characteristics of the decomposition reaction, it was impossible to achieve reaction temperatures approaching the theoretical values. This is primarily due to the effects of the wall on the reaction. Since, for nearly all cases, virtually complete decomposition was obtained in this temperature range and pressure level, acceleration of the reaction does not appear to be a significant problem. On the other hand, a more severe problem is encountered in equipment design due to the relative inability to control the reaction; however, for several experiments with pure nitrous oxide, a completely self-sustaining reaction was obtained without the use of any type of auxiliary reactor.

Experiments with  $N_2O + .88N_2$  indicate that the amount of nitrogen dioxide formation may not be significantly great to prevent further consideration for use in a wind tunnel. Further experiments should be conducted for cases of more nearly adiabatic conditions to maximize the reaction temperature.

The observed spectra from the decomposition reaction show the presence of a continuum background, with the presence of absorption bands. The absorption bands correspond to nitrogen dioxide absorption, while the continuum is due either in total to the hot nitrogen dioxide radiation or a combination of hot nitrogen dioxide radiation and nitrogen dioxide fluorescence.

The reaction rates for nitrous oxide,  $N_2O$  + .88N<sub>2</sub>, based  $N_2O$  + AIR appear to follow the following scheme

 $k_{N_20} > k_{N_20} + .88_{N_2} > k_{N_20} + AIR$ 

based on indirect observations of the temperature rise during the reactions.

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### APPENDIX I

The adiabatic flame temperature for the equilibrium reaction

$$N_20 \rightarrow N_2 + a 0_2 + b 0$$

was calculated for pressures of 1, 10, 100 atmospheres and for the case b = 0,  $a = \frac{1}{2}$ . For an adiabatic system, we have

$$n_{N_2O}^{b} \Delta H_f \qquad - \sum_i n_i^{a} \Delta H_f \qquad = 0$$

$$\frac{T/T_{b}}{\eta_{N}^{t}} \Sigma \eta_{1} \left(\frac{\Delta H_{f}}{R_{T}}\right)^{1,T} - \frac{1}{2} \left(\frac{\Delta H_{f}}{R_{T}}\right)^{N_{2}0, T_{b}} = 0$$

$$\eta_{\rm N}^{\rm t} = 2 \, \frac{{\rm n}_{\rm N20}^{\rm b}}{{\rm n}^{\rm a}}$$

where

$$\eta \quad \text{is the mole fraction}$$

$$n_{1} \quad \text{is the specific molality of species i} \left( \frac{\text{moles of i}}{\text{gram of mixture}} \right)$$

$$T_{b} \quad \text{is the temperature before reaction } \binom{o_{K}}{}$$

$$T_{a} \quad \text{is the temperature after reaction } \binom{o_{K}}{}$$

$$\Delta H_{f}^{T,i} \quad \text{is the heat of formation of species i at the indicated}$$

temperature 
$$\left(\frac{\text{calories}}{\text{gram of mixture}}\right)$$

The equilibrium reaction for the dissociation of  $O_2$  is  $1/2 O_2 \rightarrow 0$  and the equilibrium constant can be given as

$$K_0 = \sqrt{\frac{P_0}{P_{02}}}$$

The values for the thermodynamic function used in these calculations were obtained from Refs. 22 and 23. This method leads to an iterative or graphical type solution for the temperature, based on the equilibrium products at the various pressures and temperatures.

The adiabatic decomposition temperature was calculated also for the reaction

$$N_20 + .88N_2 \rightarrow 1.88N_2 + .50_2$$

by evaluating the equation

$$\frac{T}{T_{b}} \left\{ 1.88 \left( \frac{\Delta H_{f}}{R_{T}} \right)^{N_{2}, T} + 0.5 \left( \frac{\Delta H_{f}}{R_{T}} \right)^{O_{2}, T} \right\} - \left\{ \left( \frac{\Delta H_{f}}{R_{T}} \right)^{N_{2}O, T_{b}} + 0.88 \left( \frac{\Delta H_{f}}{R_{T}} \right)^{N_{2}, T_{b}} \right\} = 0$$

The results of these calculations are presented in Fig. 6. It can be seen that the theoretical temperature rise for the case of no dissociation for the pure N<sub>2</sub>O decomposition is approximately  $1600^{\circ}$ K, while for the reaction, N<sub>2</sub>O + .88N<sub>2</sub>, the temperature rise is approximately  $1000^{\circ}$ K.

### APPENDIX II

### CALCULATION OF RESIDENCE TIME AND RATE CONSTANT

The approximate residence time of the gas in the heater can be calculated as shown below

 $\Upsilon_{R} = \frac{L}{u} \qquad (sec) \qquad (1)$ 

where

 $\gamma_{\rm R}$  is the residence time

L is the length of the heater

T is the average linear gas velocity

By continuity,

$$\overline{u} = \frac{m}{\overline{\rho} A}$$
  $\left(\frac{cm}{sec}\right)$  (2)

where

m is the mass flow rate 
$$(gm/sec)$$
  
 $\overline{\rho}$  is the average density  $(gm/cm^3)$   
A is the cross-sectional area  $(cm^2)$ 

$$\mathbf{m} = \mathbf{m}(\frac{\mathbf{v}}{22.4}) \qquad \qquad \left(\frac{gm}{sec}\right) \qquad \qquad (3)$$

and

$$\overline{P} = \frac{P}{(\frac{R}{R}) \overline{T}} \qquad \left(\frac{e^{2\pi}}{cm^3}\right) \qquad (4)$$

or

$$\overline{u} = \frac{R \mathcal{V}^{T}}{22.4 \text{ p A}} \qquad \left(\frac{\text{cm}}{\text{sec}}\right) \qquad (5)$$

where

$$V \text{ is the volume flow rate at standard conditions} (liters/sec)$$

$$\overline{T} \text{ is the average temperature} \qquad (^{O}K)$$

$$R \text{ is the Universal gas constant} - 82.06 \qquad (\frac{(atm) (cm^3)}{(gm mole) (^{O}K)})$$

$$p \text{ is the pressure} \qquad (atm)$$

For a pressure level of 11.2 atmospheres and a tube diameter of 2.5 cm, the expression for the average velocity is

$$\bar{u} = .0655 \quad \tilde{V} = \left(\frac{cm}{sec}\right) \tag{6}$$

A flow rate of 3.76 liters/second, tube length of 91.5 cm, and temperatures of 1089 and 1158°K leads to residence times of .34 and .32 seconds, respectively. The corresponding concentration ratios

 $\frac{(N_2O)_a}{(N_2O)_b}$  of N<sub>2</sub>O after and before the reaction for the above conditions

is .289 and .0342, respectively.

Assuming a first order reaction, the decomposition of  $N_{\rm 2}{\rm 0}$  is given by

$$\frac{d (N_2 0)}{dt} = -k (N_2 0)$$

or

$$\frac{d(N_20)}{(N_20)} = -k dt$$

Integration leads to

$$\ln \frac{(N_2 0)_a}{(N_2 0)_b} = -k \Upsilon_R$$

where a, b refer to after and before, respectively.

At  $T_1 = 1089^{\circ}K$ ,

$$k_1 = 2.65$$
 (sec<sup>-1</sup>)

At T<sub>2</sub> = 1158°K,

$$k_2 = 10.8$$
 (sec<sup>-1</sup>)

The reaction rate constant is given by the expression

$$k = ce^{-Ea/R} T$$
(7)

or

$$\frac{\kappa_1}{\kappa_2} = \exp\left\{\frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right\} = \exp\left\{\frac{Ea}{R}\left(\frac{1}{1158} - \frac{1}{1089}\right)\right\}$$
(8)

Evaluation of (8) gives

Ea = 51,000 cal/mole

Substituting back into (7) and solving for c yields

 $c = 4.15 \times 10^{10}$ 

and the final result is

$$k = 4.15 \times 10^{10} \exp \left\{-\frac{51,000}{R}\right\}$$







SYMBOLIC DIAGRAM OF TEMPERATURE CONTROL SYSTEM FIGURE 2.



MI - 6" DIA., 48" FOCAL LENGTH FRONT SURFACE PARABOLIC MIRROR

M2, M3, M4 PLANE FRONT SURFACE MIRRORS

LI- 24" FOCAL LENGTH LENS

JA - JARRELL-ASH 21' GRATING SPECTROGRAPH

FIGURE 3. SPECTROGRAPHIC DIAGRAM

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SPECTRA OF STARTING AND STABLE DECOMPOSITION REACTION SPECTROGRAPH JARRELL - ASH FIG. 4

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FIG. 5 SPECTRA OF STABLE DECOMPOSITION REACTION BAUSCH & LOMB SPECTROGRAPH





INITIAL VS FINAL TEMPERATURE

TABLE I

DECOMPOSITION	LITERS/SEC
OXCIDE	- 1.0
TROUG	RATE
IN IN	FLOW
P	

Probe <sup>1</sup> Location	Temperature Before	Temperature After	Temperature Rise	Froducts of	f Decomposition	:
	( <sub>0</sub> K)	( <sub>No</sub> )	(y <sub>o</sub> )	Equilibrium Mixthre	at Room Tempera	• N20 tture)
4.	878	8 8 8 8 8 8 8	1 1 1 1 1 1	NO DECOMPOSITIFICM		
t.	936	7111	181			
t	950	1100	150		5.4	•
4	978	1195	211		0.00	9
4	1053	5911		00.44 27.80	2.70	9
4	1033	COTT	OTT.	00.03 27.15	6.82	ç
-1			123	66.92 27.27	5.85	-
• •		11/11	109	AIR CONTAMINA	NT IN SAMPLE	•
<b>n</b> n	760	6 3 8 8 8 8		NO DECOMPOSITION		1
0,0	220		N	IO DECOMPOSITION		
n	1019	THILL I	125	66.60 27.4B	5 27	
Ϋ́) (	1072	9811	411	67.72 27.65	10.1	
nc	200	1228	ות	67.17 27.41	5 40	
NC	020		N	O DECOMPOSITION		
N C	176		N	O DECOMPOSITION		
N C	18	1233	266	67.45 28.60	2 70	
N	1039	1278	239	66.93 27.91	21.0	00
N ·	2601	1531	205	66.59 28.03	100	5.0
	203	1311	528	64.31 28.30	20.0	5
-1 -	TT2	1172	100	65.77 28 LE		÷
	838		×	O DECOMPOSITION	<b>1</b>	<u>.</u>
-	998	1941	595	66.57 28.07	l 2A	1 2
-	916	1440	534	66.06		8.
					4.13	2
£ 7	Probe location ref	ers to position o	f probe at exit	of heater sections nu	mbered downstrea	E

TABLE II

# FURE NITROUS OXIDE DECOMPOSITION FLOW RATE - 1.5 LITTERS/SEC

(Mo)		DATA		
	(Mo)	( <sub>M</sub> o)	<pre>% N2 % O2 (Equilibrium Mixture</pre>	\$ NO <sub>2</sub> \$ 1 t at Room Temperatu
934 202	1097		O DECOMPOSITION	
1988			10 DECOMPOSITION	50.4
1025	1180	164	67.69 28.05	4.26
1075	1233	158	65.40 27.32	5.66
<u>9</u> 55		N	O DECOMPOSITION	00.0
1013	1172	M	0 DECOMPOSITION	
2/0T	1250	178	67.26 27.71	7.49
855		M	66.40 26.94	6.66
116			DECOMPOSITION	
1036	1366	361	65.98 27.90	6.06
1011	1372	295	65.55 27.36	60.7
183		ON	DECOMPOSITION	
838		569 	66.33 28.72	4.68
861 916	1527 1566	666 650	LT.82 IL.99	4.86

29

TABLE III

# FURE NITROUS OXIDE DECOMPOSITION FLOW RATE - 2.0 LITERS/SEC

Probe- Location	Temperature Before	Temperature After	Temperature Rise	Produc \$ No	ts of Decomposit	ition 4 m	Q
	( xo)	(No)	(oK)	(Equilibrium	Mixture at Room	n Temperatu	ure)
4	886	6 1 1 1 1 1 1		DECOMPOS TWICH			•
4	938			NOTITIO MODIA		1 1 1 1	
t	933			DECOMPOSITITON			
+	998	1200	212	68.73	27 Ks 3		   c
4	1050	1233	183	66.93	26 77 70	8	2
4	1079	1277	198	67.13	25.47 7	39	2 <
ŝ	922		ON	DECOMPOSITION			5
m	952			DECOMPOSITITION			
m	1019	1213	まれ	66.38	27.86 5	75	1 2
m	1072	1175	103	66.15	27.34		
m	1130	1311	181	66.04	26.81	15	
ŝ	850		ON	DECOMPOSITION			
CU I	8		ON	DECOMPOSITION			
2	772	1422	145	66.65	28.27 6.	80	4
2	1027	1394	367	65.37	27.25 7.	8	-
0	1088	1433	345	65.36	27.09 7.	55	-
	772		01	DECOMPOSITION	• •		1
	203		QU	DECOMPOSITION	1 1 1 1 1 1	1	1
-	838		01	DECOMPOSITION		1	•
-	877		01	DECOMPOSITION		1 1 1 1	
7	80	1588	688	65.95	27.45 6.0	. 09	-0

<sup>1</sup>Probe location refers to position of probe at exit of heater sections numbered downstream from inlet TABLE IV

## N20 + .88N2 DECOMPOSITION FLOW RATE - 1.88 LITERS/SEC

Probe <sup>l</sup> Location	Temperature Before	Temperature After	Temperature Rise	A N2	ts of Dec \$ 02	somposition \$ NO <sub>2</sub>	\$ N20
	(x)	( <sub>N</sub> )	( <sub>2</sub> K)	(Equilibrium )	dixture at	Rocn Tempe	irature)
4	95 C			O DECOMPOSITION	1	1 1 1 1	•
4	まち	1200	206	79.60	14.81	1.79	00
4	1056	1367	311	80.41	16.32	00.0	18
17	1103	1342	239	77.40	18.40	3.85	3 5
4	9211	1269	THI	11.17	19.65	3.24	
S	950		N	O DECOMPOSITION			1
S	981		N	DECOMPOSITION	1	•	1
S	1005	1269	263	80.02	10.81	1.82	.15
S	1067	1269	202	14.77	04.81	80.6	00
ß	1158	1350	192	17.17	18.00	01.4	5
ŝ	958		× · · · · · · · ·	DECOMPOSITION	1		1
ŝ	958			DECOMPOSITION	1 1 1	1 1 1 1	1
2	1050	6141	369	19.51	20.32	3.84	52.
2	1090	1445	355	78.21	17.92	3.70	21
N	1172	1509	337	78.21	18.25	3.52	8
Q	1230	0441	210	79.30	18.53	2.17	4
Ч	803			DECOMPOSITION	1 1 1 1	•	•
Ч	833			DECOMPOSITION	1	1	1
Ч	895		W	DECOMPOSITION	1	1 1 1 1	1
г	er Er	5 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	X	NOTITI SOMOCIAL C	1	1 1 1 1	1
Ч	1005		M N	DECOMPOSITION	1 1 1	1	1
Ч	1060			DECOMPOSITION	1	1 1 1 1	1
4	Probe location refe	rs to position of	c probe at exit o	of heater sectio	ns number	ed downstre	E.
-	from inlet						1

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TABLE V

N20 + .88N2 DECOMPOSITION FLOW RATE - 2.82 LITERS/SEC

4         950         1375         325         100 DECONFOCITION         16.67         3.91           11111         12297         1366         79.39         16.67         3.91           1125         1450         325         79.31         16.67         3.91           1125         1450         325         79.31         16.67         3.91           1125         1450         325         79.31         16.67         3.91           1125         1450         325         79.31         16.67         3.91           1125         1430         225         79.51         17.64         3.06           1100         1394         250         76.58         17.64         3.06           1100         14.38         250         76.51         17.61         4.25           922         14.38         250         78.61         17.61         4.25           926         1172         14.92         3.06         17.61         4.25           923         1075         14.92         3.06         17.61         4.25           928         1075         14.92         3.01         17.61         3.93           1075	5 N2 5 O2 5 M Milibrium Mixture at Room
1000       1375       325       79.39       16.67       3.91         1111       1297       186       79.82       18.01       2.17         1125       1450       325       79.32       18.01       2.17         33       978       16.67       3.91       16.67       3.91         33       978       16.01       2.17       4.92         33       1042       1394       294       76.58       17.64       3.06         1100       1394       294       76.58       17.64       3.06         1100       1100       1438       250       76.58       17.64       3.06         1100       117.61       17.61       4.25       3.06       4.25       3.06       4.25         201       2050       76.61       17.64       3.93       3.06       4.25       3.06         201       205       76.61       17.64       3.93       3.06       4.25       3.93       3.06         201       205       76.61       17.64       3.93       3.06       4.25       3.93       3.93       3.93       3.93       3.93       3.93       3.93       3.93       3.93       3	MPOSITITION NOTITI SORM
1050       1375       325       79.39       16.67       3.91         1111       1297       1450       325       79.39       16.67       3.91         33       933       978       1450       325       79.39       16.67       3.91         3       933       978       1450       325       76.31       16.77       4.92         3       1042       1394       294       76.58       17.64       3.06         3       1156       1436       294       76.58       17.61       4.92         967       922       76.61       17.64       3.06       17.64       3.06         967       1075       1436       250       76.58       17.64       3.06         967       1436       250       76.61       17.64       3.06         967       1436       250       76.51       17.64       3.05         967       1262       341       76.51       17.61       3.93         968       1262       341       76.51       17.61       3.93         963       1262       341       70.31       17.61       3.93         964       1262       <	MPOSTTTON
1111       1297       166       79.82       16.01       2.17         978       933       946       325       76.31       16.77       4.92         33       1042       1394       294       76.58       17.64       3.06         33       1156       1438       294       76.58       17.64       3.06         33       1156       1438       250       78.61       17.64       3.06         967       83.61       77.64       3.06       77.64       3.06         978       1000       1438       250       78.61       17.64       3.06         978       117.64       3.06       78.61       17.64       3.93         982       1075       1499       327       79.31       17.64       3.93         1075       1499       327       79.31       17.64       3.93         1075       1499       327       79.31       17.64       3.93         1172       1499       327       79.31       17.64       3.93         1075       1499       327       79.31       17.64       3.93         1076       17.64       3.93       17.64       3	19.30 16.67 3
1125       1450       35       78.31       16.77       4.92         33       978       933       933       933       933       933         978       1004       1394       294       10.0000005171001       10.01         11000       1394       294       17.64       3.06         967       967       78.61       17.64       3.06         967       967       78.61       17.64       3.06         967       967       78.61       17.64       3.06         967       967       78.61       17.64       3.06         967       967       78.61       17.64       3.06         968       1075       1499       327       78.05       17.64       3.93         1077       1172       1499       327       78.05       17.64       3.93         1172       1499       327       78.05       17.64       3.93         11222       1499       327       78.05       17.64       3.93         1222       1222       1499       78.05       17.64       3.93         1222       1222       1499       79.05       17.64       3.93 <td></td>	
933       933       933       933         976       042       1042       17.64       3.06         1100       1394       294       76.58       17.64       3.06         978       1156       14.36       76.56       17.64       3.06         922       922       78.61       17.64       3.06         923       924       76.56       17.64       3.06         925       927       10.0       17.61       4.25         926       1075       14.99       327       78.05       17.64       3.93         1075       1172       14.99       327       78.05       17.64       3.93         1172       1149       327       78.05       17.64       3.93         1172       1149       327       79.31       17.64       3.93         1222       1562       34.1       79.31       17.64       3.93         1222       1562       34.1       79.31       17.64       3.93         1222       1562       34.1       79.31       17.64       2.80         923       933       93.1       17.64       3.93       17.64       2.80	10.21 16.77 L
978       1042       1394       294       76.58       17.64       3.06         1100       1436       294       76.58       17.64       3.06         922       922       78.61       17.64       3.06         967       967       78.61       17.61       4.25         967       967       78.61       17.61       4.25         967       967       967       78.61       17.61       4.25         967       967       967       78.61       17.61       4.25         967       967       967       78.61       17.61       4.25         967       967       967       96       96       96       96         968       1075       1499       327       78.05       17.64       3.93         1172       1499       327       78.05       17.64       3.93         1222       1562       34.1       79.31       17.64       3.93         1222       1562       34.1       79.31       17.64       3.93         1222       1562       34.1       79.35       17.64       3.93         1222       1562       34.1       79.31	NOILISOUM
3       1042       1394       294       76.58       17.64       3.06         3       1156       1436       250       76.58       17.64       3.06         922       922       78.61       17.61       4.25         967       967       76.56       17.64       3.06         967       967       78.61       17.61       4.25         967       967       969       78.61       17.64       3.93         967       967       960       960       960       963       963         1075       1172       1499       327       78.05       17.64       3.93         1075       1172       1499       327       78.05       17.64       3.93         1075       1172       1562       34.1       79.31       17.87       2.80         825       1562       34.1       79.31       17.87       2.80         833       12222       1562       34.1       79.31       17.87       2.80         826       1266       34.1       79.31       17.87       2.80         933       12222       1562       34.1       79.31       17.87       2.80	MPOSITION NoITISOTM
3       1100       1394       294       76.58       17.64       3.06         922       922       922       78.61       17.64       3.06         967       78.61       17.64       3.06         967       961       1436       250       76.56       17.64       3.06         967       967       960       78.61       17.64       3.06         967       967       960       78.05       17.64       3.93         968       1172       1499       327       78.05       17.64       3.93         91075       1499       327       78.05       17.64       3.93         925       1222       1499       341       79.31       17.87       2.80         926       1262       341       79.31       17.64       3.93         922       1562       341       79.31       17.61       2.80         923       933       934       79.31       17.61       2.80         922       1262       341       79.31       17.61       2.80         923       933       94       79.31       17.61       2.80         924       925       <	MPOSITION NOTTI SOM
3       1156       1438       250       78.61       17.61       4.25         967       967       967       961       10.661       4.25         967       967       967       967       967       967         967       967       967       967       967       967         967       967       967       967       967       967         967       10058       967       967       967       967         10075       10075       1499       327       78.05       17.64       3.93         10075       1172       1499       327       78.05       17.64       3.93         1172       1178       17.64       3.93       17.64       3.93         1172       1562       34.1       79.31       17.64       2.80         118       884       984       9.31       17.64       2.80         119       925       933       9.31       17.64       2.80         11       922       93       9.31       17.64       2.80         11       922       93       9.31       17.64       9.31         10       920       9	6.58 17.64 3
922       922         967       967         961       1058         1058       10         1172       1499         1172       1499         1222       1499         1222       1499         1222       17.64         1222       1562         1222       78.05         1222       17.64         825       34.1         833       79.31         84       79.31         82       79.31         82       94         92       94         933       94         92       94         93       94         93       94         94       79.31         92       94         93       94         94       95         94       95         95       96         96       97.81         97.91       97.91         98       98         98       98         98       98         98       98         98       98         98       98	8.61 17.61 h
907       907       907       907       907         1056       1075       10       DECOMPOSITION       90         1075       1075       1499       327       78.05       17.64       3.93         1172       1499       327       78.05       17.64       3.93         1222       1499       327       78.05       17.64       3.93         1222       1562       34.1       79.31       17.64       2.80         1223       1562       34.1       79.31       17.64       2.80         1223       1562       34.1       79.31       17.64       2.80         1224       1562       34.1       79.31       17.64       2.80         1225       1562       34.1       79.31       17.64       2.80         1226       17.64       9.05       17.64       3.93       2.93         1222       1562       34.1       79.31       17.64       2.80         1222       1262       34.1       79.31       17.64       2.80         1222       1262       34.1       79.31       17.64       2.80         1222       1262       16       16.1	NOLLI SOUN
2       1075       1499       327       78.05       17.64       3.93         2       1172       1499       327       78.05       17.64       3.93         2       1222       1499       327       78.05       17.64       3.93         2       1222       1499       327       78.05       17.64       3.93         8       1222       1562       34.1       79.31       17.64       2.80         8       833       1562       34.1       79.31       17.64       2.80         8       833       1562       34.1       79.31       17.64       2.80         8       833       1562       9.1       79.31       17.64       2.80         9       804       10.000000517100       17.61       2.80         9       10000       10000000517100       17.61       17.61         9       10000       10000000517100       17.61       17.61         9       10000       10000000517100       17.61       17.61         9       10000       10000000517100       17.61       17.61         100000       10000000517100       10.00000000000       10.0000000000000000000000000000000	NOILISOUM
2       1172       1499       327       78.05       17.64       3.93         2       1222       1499       327       78.05       17.64       3.93         2       1222       1562       341       79.31       17.64       3.93         1       825       1562       341       79.31       17.64       3.93         1       825       1562       341       79.31       17.87       2.80         1       833       12.22       17.64       3.93       17.64       3.93         1       825       17.66       34.1       79.31       17.87       2.80         1       833       12.22       17.64       3.93       17.64       3.93         1       833       17.65       70       17.67       2.80         833       10.00000000000000000000000000000000000	NOLLISOUM
2       1172       1499       327       78.05       17.64       3.93         2       1222       1562       341       79.31       17.64       3.93         1       825       1562       341       79.31       17.87       2.80         1       833       1       79.31       17.64       3.93         833       1       79.31       17.87       2.80         833       1       79.51       2.00       2.60         833       1       79.51       2.00       2.60         833       1       79.51       17.64       3.93         833       1       79.51       2.60       2.60         833       1       17.64       3.93       2.60         833       1       17.64       17.64       2.60         833       1       17.67       17.08       17.64         922       1       10.00       10.00       10.00       10.00         1       1000       10.00       10.00       10.00       10.00       10.00         1       1000       10.00       10.00       10.00       10.00       10.00	MPOSITION NOITI SOM
2       1222       1562       34.1       79.31       17.87       2.80         1       825	8.05 17.64 3.
025       00       DECOMPOSITION       0         033       034       0       DECOMPOSITION       0         084       0       0       0       0         084       0       0       0       0         080       0       0       0       0         081       0       0       0       0         082       0       0       0       0         081       0       0       0       0         082       0       0       0       0         083       0       0       0       0         080       0       0       0       0         080       0       0       0       0         080       0       0       0       0         080       0       0       0       0         080       0       0       0       0         080       0       0       0       0         080       0       0       0       0         080       0       0       0       0         080       0       0       0       0       0	9.31 17.87 2.4
1       033       NO       DECOMPOSITION	NOLLISOUM
1       922       -       -       -       -       -       NO       DECOMPOSITION       -	MPOSITION
1   922	NOLLISOUM
	MPOSITION NOITISOTM
	MPOSITION NOITISOTM
	MPOSITION NOITISON

# M20 + .88M2 DECOMPOSITION

SEC
LITTERS
3.76
RATE
HOTH

$(\mathbf{r},\mathbf{r})$ $(\mathbf{r},$	Probe <sup>1</sup> Location	Temperature Before	Temperature After	Temperature Rise	Froducts of Decomposition \$ N <sub>2</sub> \$ 0 <sub>2</sub> \$ N0 <sub>2</sub> \$ N <sub>2</sub> 0
4       942       942         647       1056       1428       317       79.17       17.13       3.70       -0-         1111       1426       317       79.17       17.13       3.70       -0-         33       931       79.17       17.13       3.70       -0-         33       931       79.27       16.06       4.69       -0-         33       933       931       79.25       16.06       4.69       -0-         33       933       933       934       79.25       16.06       4.69       -0-         33       933       933       934       79.25       16.06       4.69       -0-         34       1033       1183       25       N0 DECORPOSITION       -0       17.13       3.70       -0-         35       1183       25       N0 DECORPOSITION       -0       17.52       2.71       1.43         1048       1183       25       N0 DECORPOSITION       -0       1.43       -0         1184       1510       323       76.64       1.75       2.77       1.43         1184       1510       323       76.64       1.75       2.77		(MC)	( <sub>2</sub> )	(vr)	(Equilibrium Mixture at Room Temperature)
44       947       1056       14.48       317       79.17       17.13       3.70       -0-         11111       11464       314       79.17       17.13       3.70       -0-         3       931       79.17       17.13       3.70       -0-         3       931       79.25       16.06       4.69       -0-         3       933       1103       11       79.17       17.13       3.70       -0-         3       931       78.55       16.06       4.69       -0-       -       -       -0-         3       1033       1100       1100       11       69.51       14.93       5.09       1.43         3       1069       1100       11       69.55       14.93       5.09       1.43         1158       1158       78.55       14.93       5.09       1.43         1164       1100       12000FOSTTION       -       -       -         1158       1168       11.66       14.93       5.09       1.43         1158       1168       1100       12.00       1.43       1.43       1.43         1164       1168       16.55       14.93 <td>ŧ</td> <td>942</td> <td></td> <td>01</td> <td>DECOMPOSITION</td>	ŧ	942		01	DECOMPOSITION
4       1056       1111       14-26       317       79-17       17-13       3.70       -0-         3       931       14-64       314       79-25       16.06       4.69       -0-         3       975       14-64       314       79-25       16.06       4.69       -0-         3       975       14-64       314       79-25       16.06       4.69       -0-         3       975       14-93       51       17-13       3.70       -0-         3       1033       1100       10000000517101       -1       14.33       64         3       1069       1100       25       14-93       5.09       1.43         3       1069       1100       25       14-93       5.09       1.43         3       1046       10000000517101       -1       1.43       5.09       1.43         945       1184       1510       323       25       14-93       5.09       1.43         1048       1188       1510       323       78.64       17.52       2.77       1.07         1184       1510       323       1510       323       78.64       17.52       2.7	4	5		ON	DECOMPOSITION
4       1111       14/26       317       79.17       17.13       3.70       -0-         3       931       1464       314       79.25       16.06       4.69       -0-         3       975       1464       314       79.25       16.06       4.69       -0-         3       975       1464       314       79.25       16.06       4.69       -0-         3       1033       11003       11       69.51       12.41       4.44       13.64         3       1069       1100       10000005070000517100       -       -       -       -       -       -         3       1069       1103       25       14.93       5.09       1.43       -       -         3       1048       -       -       NO       DECONFOSTTION       -<	4	1056		QN	DECOMPOSITION
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4	IIII	1428	317	79.17 17.13 3.70 -0-
3       931       931       931         3       975       975       975         3       1033       1100       11       69.51       12.41       4.44         3       1069       1100       11       69.51       12.41       4.44       13.64         3       1069       1163       25       78.55       14.93       5.09       1.43         2       942       942       942       94       14.93       5.09       1.43         2       942       942       94       17.52       2.7       14.93       5.09       1.43         2       942       94       17.52       2.77       14.93       5.09       1.43         2       94       94       17.52       2.77       1.43       1.43         2       1184       17.52       2.77       1.07         825       1233       1510       323       78.64       1.07         876       1233       1510       323       78.64       17.52       2.77       1.07         1       945       17.52       2.77       1.07       1.07       1.07       1.07         1	t	1150	1941	314	79.25 16.06 4.69 -0-
3       975	m	931		ON	DECOMPOSITION
3       1033       1100       11       69.51       12.41       4.44       13.64         3       1158       1163       25       78.55       14.93       5.09       1.43         8       942       1163       25       78.55       14.93       5.09       1.43         942       942       10048       11.63       76.55       14.93       5.09       1.43         2       942       10048       10.000       10.000       14.93       5.09       1.43         2       942       1048       11.64       11.64       11.43       1.43         2       1048       11.184       11.64       17.52       2.77       1.07         2       1233       1510       323       78.64       17.52       2.77       1.07         1       816       17.52       2.77       1.07       1.07         1       825       164       17.52       2.77       1.07         1       945       17.52       2.77       1.07         1       816       17.52       2.77       1.07         1       945       17.52       2.77       1.07         1	m	975		ON	DECOMPOSITION
3       1069       1100       11       69.51       12.41       4.44       13.64         2       866       1163       25       78.55       14.93       5.09       1.43         2       942       1046       1000       1000       14.93       5.09       1.43         2       942       10046       1000       14.93       5.09       1.43         2       1046       1000       16.55       14.93       5.09       1.43         2       1046       1000       1000       14.93       5.09       1.43         2       1046       17.52       14.93       5.09       1.43         2       1184       17.52       2.77       1.07         1184       12.510       323       78.64       17.52       2.77       1.07         1233       1510       323       78.64       17.52       2.77       1.07         1233       1510       323       78.64       17.52       2.77       1.07         1233       1510       323       78.64       17.52       2.77       1.07         1233       1510       323       78.64       17.52       2.77       <	m	1033		ON	DECOMPOSITION
3       1158       1183       25       78.55       14.93       5.09       1.43         2       942       1048       104.93       5.09       1.43         2       942       104.93       5.09       1.43         2       942       104.93       5.09       1.43         2       1048       1048       107       107         2       133       1510       323       78.64       17.52       2.77       1.07         1       825       1510       323       78.64       17.52       2.77       1.07         1       876       103600000000000000000000000000000000000	m	1089	1100	11	69.51 12.41 4.44 13.64
2       086	S	1158	1183	25	78.55 14.93 5.09 1.43
2       942	N	886		01	DECOMPOSITION
2       10046	S	942		ON NO	DECOMPOSITION
2       1184	N	1048		01 10	DECOMPOSITION
2       1233       1510       323       78.64       17.52       2.77       1.07         1       816	2	1811	•	01 100	DECOMPOSITION
1       B16       • • • • • • • • • • • • • • • • • • •	2	1233	1510	323	78.64 17.52 2.77 1.07
1       825       • • • • • • • • • • • • • • • • • • •	Ч	816		01	DECOMPOSITION
1       878	1	825		01	DECOMPOSITION
1 945	Ч	878		ON	DECOMPOSITION NOITI SOMMOSIT
1 1003	1	572		01	DECOMPOSITION
	Ч	1003		01	DECOMPOSITION
		LIOM INTEL			

		N20	+ ALR DECOMPOSIT	NOL			
Probe <sup>1</sup> Location	Temperature Before ( <sup>o</sup> K)	Temperature After ( <sup>o</sup> K)	Temperature Rise ( <sup>O</sup> K)	Produc	cts of De \$ 0 <sub>2</sub> Mixture	composition \$ NO <sub>2</sub> at Room Temp	\$ N <sub>2</sub> 0 erature)
		Total Flo	v Rate - 2.0 Lit	ers/Sec			
<i>4444</i>	962 1005 11478	1370 1311 1286 1293	408 306 145	71.02 70.46 70.33 70.94	26.24 25.07 25.45 25.45	2.38 3.34 3.38 3.38 45 8 3.38 5 8 3.38 5 8 5 8 5 8 5 8 5 8 5 8 5 8 5 8 5 8 5	900 88 88 77
		Total Flo	w Rate - 3.0 Lit	ers/Sec			
オオオ	950 1014 1072			DECOMPOSITION DECOMPOSITION		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1 1 1 1 1 1 1 1 1 1 1
-т °	Probe location refe from inlet	ars to position of	f probe at exit (	of heater secti	ons numbe	red downstre	am

TABLE VII

34