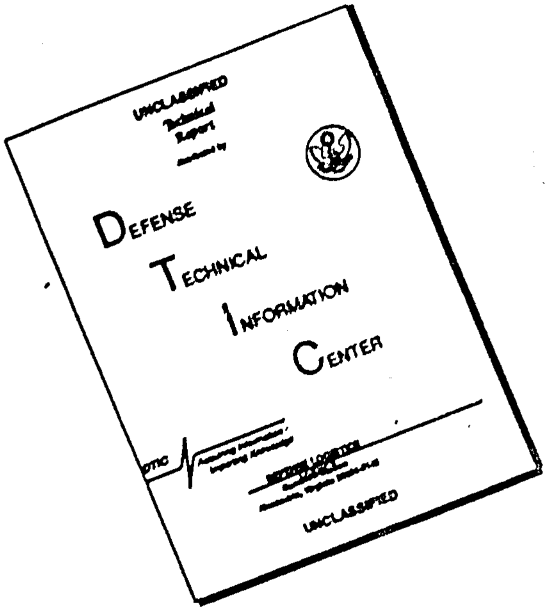

ARL 62-430

CHEMICAL KINETICS OF NITROUS OXIDE DECOMPOSITION AT ELEVATED PRESSURES AND TEMPERATURES

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SEPTEMBER 1962

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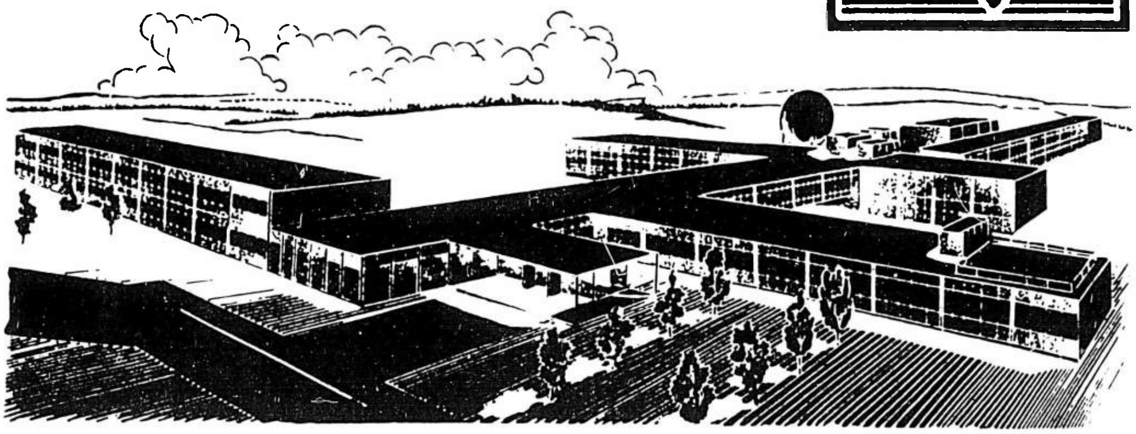

NOTICES

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FOREWORD

This technical documentary report was prepared by E. Stokes Fishburne and Rudolph Edse of the Department of Aeronautical and Astronautical Engineering of The Ohio State University on Contract Number AF 33(616)-5615, 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 Aeronautical Research Laboratories, Office of Aerospace Research, Wright-Patterson Air Force Base, Ohio, with Mr. Robert G. Dunn, Fluid Dynamics Facilities Laboratory, as Project Scientist.

This report covers one phase of the investigation on Contract AF 33(616)-5615. Future studies on the kinetics of the decomposition of nitrous oxide using high-speed spectroscopic techniques will be conducted on a succeeding contract.

ABSTRACT

Kinetic studies of the thermal decomposition of nitrous oxide were conducted in the temperature range from 1000 to 2500°K. The decomposition of nitrous oxide behind the reflected shock wave in a shock tube was investigated using photographic techniques. It appears that the rate of decomposition may be governed by the vibrational relaxation time of the lower energy valence bond. Induction times for the rapid decomposition of nitrous oxide range from 152 microseconds at 1430°K to zero microseconds at about 2500°K. The value of about 150 microseconds at 1430°K agrees qualitatively with approximate values obtained by other investigators.

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LIST OF SYMBOLS

E	Internal energy
E_o	Zero point energy
h	Absolute enthalpy per unit mass
H_T	Absolute molar enthalpy at temperature T
$\left(\frac{H-E_o}{\mathcal{R}T}\right)_T$	Reduced enthalpy at temperature T
$\mathcal{M}$	Molecular weight
n	Mole number per unit mass of mixture
p	Absolute pressure
T	Absolute temperature
u	Velocity
ρ	Density
θ^i_{vib}	Characteristic temperature of the ith vibrational mode of nitrous oxide

SUBSCRIPTS

1	Initial conditions of nitrous oxide
2	Conditions of nitrous oxide behind normal shock wave (driven gas)
3	Conditions of driver gas behind contact surface
4	Initial conditions of driver gas
p	Particle conditions behind the incident shock wave
r	Conditions of nitrous oxide behind reflected shock wave

SECTION I

INTRODUCTION

It has been proposed to use nitrous oxide as an energy source for high enthalpy flow wind tunnels needed for the simulation of hypersonic flight vehicle tests. To obtain proper flow conditions it is necessary to understand the rate and mechanism of the decomposition of this endothermic compound at elevated temperatures and pressures. Under these conditions the reaction rate of the decomposing nitrous oxide, forming nitrogen and oxygen, is extremely rapid. Previous experimental work performed at pressures near one atmosphere by Hunter (Ref. 1) indicates that, at a temperature of about 1000°K, the decomposition rate increases by about 48 per cent with each 25°K increase in temperature.

The experimental methods required for the study of chemical reaction rates and mechanisms depend greatly on the magnitude of the rate. Reactions having a half life of about five seconds for the reactant are considered to be slow. Under these conditions no real difficulties are encountered in making measurements. When the half-life period ranges between five and 0.05 seconds, the rates are considered moderately fast and it becomes somewhat difficult to make rate studies by conventional methods. If half lives of less than 0.05 second are involved, the reactions are very rapid and new methods are needed to determine the reaction rate constants. Under these conditions it is imperative to reach the desired operating temperature of the reacting system almost instantaneously.

Previously (Ref. 2) it was shown that, at temperatures below about 1000°K and at moderate pressures, a heated constant-volume vessel could be used for measuring the decomposition rate of nitrous oxide. However, when the pressure was raised, the reactions led to explosive decomposition. Under these conditions this technique did not yield any reliable information on the reaction rate. Therefore, this method of measurement was abandoned and other techniques were investigated.

One of the first problems encountered in the study of the decomposition rate of nitrous oxide was the scarcity of thermodynamic data which went only to 1500°K (Ref. 3). Since information was needed at much higher temperatures, it was necessary to calculate the enthalpy of nitrous oxide up to 3000°K. The manner in which this calculation was performed and the resulting data are given in Appendix I.

Note: Manuscript released in April 1962 by the authors for publication as an ARL Technical Documentary Report.

SECTION II

REACTION RATES DERIVED FROM MEASUREMENTS OF BURNING VELOCITIES

If the mechanism of the reaction kinetics in a combustion wave can be established, it is possible to derive reaction rate constants from measurements of burning velocities. In general, the interpretation of these measurements is rather complex and not free from errors. In spite of these shortcomings this technique was investigated primarily because of the relatively simple kinetics of the decomposition of nitrous oxide.

The existence of decomposition flames has been demonstrated experimentally by Friedman and Burke (Ref. 4), Adams and Stocks (Ref. 5), and Parker and Wolfhard (Ref. 6). A steady decomposition flame of hydrazine, which releases 33,000 calories per mole upon decomposition, was obtained by Adams and Stocks. Friedman and Burke obtained an ethylene oxide decomposition flame. Ethylene oxide releases either 32,000 or 8,000 calories per mole depending on the mechanism of decomposition. However, the most interesting decomposition flame, from the point of view of this study, is the nitric oxide decomposition flame obtained by Parker and Wolfhard. Nitric oxide releases about 20,000 calories per mole upon decomposing.

Henkel, Spaulding, and Hirschfelder (Ref. 7) applied a theory advanced by Adams (Ref. 8) to predict the conditions under which a decomposition flame of nitric oxide could be obtained. According to Henkel, et al., the nitric oxide must be preheated to about $1000^{o}K$ and the flame started in such a manner that the resultant flame temperature is about $3000^{o}K$. Parker and Wolfhard, using this information, preheated the nitric oxide to about $1000^{o}K$ and started the flame with hydrogen. The resultant hydrogen - nitric oxide flame temperature was in excess of $3000^{o}K$. The flame was prevented from flashing back by quartz chips in the burner tube. These quartz chips also aided in heating the gas by transferring the heat more readily because of additional surface area. When the hydrogen was removed the decomposition flame of nitric oxide remained.

On the basis of this theory it was determined that the nitrous oxide should be preheated to a temperature of about $700^{o}K$ and the flame should be started by adding a fuel so that the resultant mixture would have a flame temperature which is somewhat higher than $2300^{o}K$. A steady decomposition flame of nitrous oxide, which had been preheated to an initial temperature of about $700^{o}K$, would have an adiabatic flame temperature of about $2200\text{-}2300^{o}K$ at a mass flow rate per unit burner area of about 0.015 gm/cm^2sec. For a detailed discussion of this method, the reader is referred to References 7 and 8.

A Bunsen-type burner was constructed which allowed the nitrous oxide to be heated to temperatures near 1200°K. Pebble-sized pieces of silica brick were used to fill most of the tube to aid in the heating and as a precaution against flash-back. To initiate the decomposition flame, mixtures of hydrogen - nitrous oxide, carbon monoxide - nitrous oxide, and ammonia - nitrous oxide were tried eventually. According to Parker and Wolfhard (Ref. 6), these mixtures have burning velocities of 400, 20 and 80 cm/sec respectively when the gases are at room temperature initially. Although greater burning velocities will result at higher initial gas temperatures, it appears that a pure decomposition flame whose burning velocity is only 15 cm/sec can be stabilized when the additive is withdrawn.

The flame temperatures of the three flames were not known. However, they were estimated to be much higher than 2400°K, since the flame temperatures of hydrogen-air, carbon monoxide - air, and ammonia-air mixtures are about 2400°K, 2400°K and 2100°K respectively when the gases are at an initial temperature of only 300°K (Ref. 9). Since nitrous oxide is an endothermic compound and its nitrogen-to-oxygen ratio is only two, it is reasonable to expect the flames of a fuel and nitrous oxide to be much hotter than the corresponding fuel-air flames. Thus, considering both conditions, it appears that a decomposition flame should be obtainable.

The burning velocities of the hydrogen - nitrous oxide and ammonia - nitrous oxide gas mixtures were evidently much too large to obtain a stable flame. When the preheated gases were ignited at the top of the burner, a considerable mass flow rate had to be maintained to prevent flash-back. As the hydrogen or ammonia was removed from the gas flow, the flame would blow off. In an attempt to keep the flame seated on the burner rim, the nitrous oxide flow rate was reduced gradually. This procedure was fairly successful until the flow rate was rather small at which time the flame would flash back. All attempts to obtain a decomposition flame with the hydrogen and ammonia were unsuccessful. Since the burning velocity of the carbon monoxide - nitrous oxide flame was very close to the predicted burning velocity of the decomposition flame, it was decided that this system would offer the best opportunity to obtain the decomposition flame.

The carbon monoxide - nitrous oxide mixture generally reacted in the pebble bed of the burner tube. To avoid this situation the temperature of the pebble bed was lowered, the flow velocity was increased and a carbon monoxide - air flame was established into which the nitrous oxide was gradually added. The result was that the carbon monoxide - nitrous oxide mixture would either react in the pebble bed or the flame would blow off as the carbon monoxide was reduced. Because of these difficulties and considering the doubtful value of the flame studies, it was decided to abandon this approach at this time in favor of the shock-tube method.

SECTION III

CHEMICAL KINETICS FROM SHOCK-TUBE STUDIES

Shock-tube techniques have been used very successfully by several investigators for the study of rapid chemical reactions (Refs. 10-14). Figure 1 shows a wave diagram of the flow phenomenon existing in a simple shock tube. Generally this diagram is used since it gives the position of each wave in the tube as a function of time. Most of the research performed in the shock tube has involved the use of the reflected shock wave. This particular wave offers the advantages that the gas remains essentially at rest, that a much higher temperature is obtained than behind the incident shock wave, and that a longer test time is available than behind the incident shock wave. The results of the calculations of the temperatures and pressures behind the incident and reflected shock wave are presented in Appendix II.

Glick, et al., (Ref. 10) have constructed a single pulse shock tube in which the gas is raised to the desired experimental temperature behind the reflected shock wave and then is cooled suddenly by the arrival of an expansion wave. The time between the arrival of the reflected wave and the arrival of the expansion wave is controlled by the rupture of two diaphragms. The first diaphragm is located between the driver gas and sample gas while the second is placed between the driver gas and a very low pressure reservoir. The bursting of the first diaphragm creates the shock wave and the expansion wave is generated by bursting the second diaphragm. The time between the bursting of the two diaphragms can be controlled to within ± 100 microseconds approximately. After the gas to be studied has been subjected to this rapid heating and quenching cycle, a sample is taken from the end of the shock tube and analyzed chemically to determine the composition. For a full discussion of this technique the reader is referred to Reference 10. The necessary alterations of the existing shock tube facility rendered this technique impractical for the present study.

The existing shock tube facility (Ref. 2) consists of a square shock tube 350 centimeters in length and 3.8 centimeters square. Two large valves, which separate the driver, buffer, and sample sections, were installed for the purpose of operating the shock tube without diaphragms. These valves were used quite successfully in a previous study in which all three sections were at the same pressure initially. However, after a series of experiments, it was determined that the high temperatures necessary for this study could not be obtained unless the driver section had a higher initial pressure than the sample and buffer sections. This condition was achieved by the reduction of the pressure in the buffer and sample gas and the installation of a 0.010-inch steel diaphragm between the driver and buffer sections. Since the shock tube was not designed originally for diaphragms, considerable time was expended to the modification and development of experimental techniques. After the changes were made, the shock strength in the sample gas was sufficient to increase the gas temperature in excess of 3000°K. The upper pressure limit at which the decomposition rate could be determined is governed by the glass windows in the tube. Since the windows did break once, it was decided to place an upper limit of about 40 atmospheres on the gas pressure behind the reflected shock wave.

The other major items used with the shock tube were the schlieren system and a rotating drum camera. The drum camera essentially produced a wave diagram of the incident and reflected shock waves on the high-speed film. From a measurement of the slope of the incident or reflected shock wave as recorded on the film and from a knowledge of the rotational speed of the film, the shock-wave velocities could be determined. These velocities then could be related to the temperature and pressure behind the reflected shock wave.

At one time during this study a very serious problem existed to synchronize passage of the shock wave with the opening of the camera shutter. This problem results from being unable to score the diaphragm in a consistent manner. The result is a slightly different bursting time for each diaphragm. However, near the close of the work, more success was attained in the consistent scoring of the diaphragm and only one shock in three or four was missed.

It can be shown that the time rate of decomposition of an endothermic compound may be related directly to an increase in the velocity of the reflected shock wave. This increase in velocity is related directly to the rate of energy release in the gas behind the reflected shock wave and thus to the rate of decomposition of the compound. It has also been shown (Ref. 15) that the rapid decomposition of nitrous oxide is accompanied by a luminescent glow. Strehlow and Cohen (Ref. 15), in their study of the reflected shock wave used nitrous oxide in one experiment and obtained a temperature of over 1400°K. A strip-film photograph of the shock-wave pattern revealed that the nitrous oxide, after an induction period, decomposed very rapidly as shown by a region of intense radiation. As shown in Section IV similar results were obtained in this study.

SECTION IV

EXPERIMENTAL RESULTS

The velocities of the incident and reflected shock waves were determined from strip-film photographs similar to those shown in Figures 2 through 5. From a series of measurements of the slopes of the shock waves recorded on the film, it was concluded that the reproducibility of the measurements is about one per cent. However, in some cases the spread of the slope measurements may deviate as much as three per cent from the average.

The results of the more reliable experiments are given in Table I. The schlieren traces for experiments 56, 57, 81 and 82 are shown in Figures 2 through 5. Experiment number 56 is particularly noteworthy since the windows in the tube cracked during this experiment. As can be seen in Figure 2, a region of very intense radiation occurred after passage of the reflected shock wave. This was the first experiment in which a region of intense radiation was obtained. From Table I it is seen that the theoretical pressure and temperature behind the reflected shock wave are 167 atmospheres and 1430°K respectively. The only possible explanation of this intense region of radiation is that the nitrous oxide decomposed in an explosive manner after an induction period of about 150 microseconds. Under such conditions of sudden energy release, the pressure and the temperature could have reached 600 atmospheres and 3000°K, respectively. A transient pressure of 600 atmospheres is sufficiently high to break the observation windows.

In Figures 2, 3 and 5 a distinct region of intense radiation can be observed at some point behind the reflected shock wave, while in Figure 4 the entire region behind the reflected shock wave is radiating rather intensely. In these three figures an induction time preceding the region of intense radiation can be measured. These induction periods are presented in Table I. It is worthy of note that experiments 56 and 82 have about the same induction time and have temperatures in the same region. A much shorter induction time was obtained in experiment 57 whereas experiment 81 had no measurable induction time. Likewise the temperatures in experiments 57 and 81 are much higher than those in experiments 56 and 82.

Careful observation of the wave structure in Figure 5 reveals what appears to be a wave of some type originating at the end of the tube about 150 microseconds after passage of the reflected shock wave. The velocity of this wave was about 1900 ± 200 m/sec. An approximate calculation indicates that the detonation velocity of nitrous oxide should be about 2000 m/sec under the conditions of temperature and pressure behind the reflected shock wave. Therefore, it appears that nitrous oxide detonated during this experiment.

The induction times mentioned in the preceding paragraphs are probably related in some manner to the vibrational relaxation time of nitrous oxide. However, the amount of data obtained thus far precludes any attempt to relate them uniquely. Griffith, et al., (Ref. 16) have reported a vibrational relaxation time of less than a microsecond for the bending mode. Their observation time was about 100 microseconds and thus relaxation times of longer duration could not be determined by them. They did, however, believe that a relaxation time at least 100 times greater than that of the bending mode was indicated by the observation that the gas behind the shock was not in thermal equilibrium. This rough approximation agrees fairly well with the present results according to which the induction time is about 150 microseconds at 1430°K. Thus, if it is assumed that the molecule must be vibrationally excited in the lower energy valence mode before dissociation occurs, then this vibrational relaxation time would place a limit on the rate of decomposition of nitrous oxide.

Figure 6 depicts the reflected shock velocity as a function of the incident shock velocity. The theoretical predictions of the reflected shock velocity, based on complete thermodynamic equilibrium, are given by the curve on the left. At first it appeared that these predictions were much too low. With an incident shock velocity of 800 m/sec the apparent reflected shock velocity obtained in the experiment was about 50 per cent higher than the predicted value. For this incident velocity the temperature behind the reflected shock is about 960°K which is much too low for the decomposition of nitrous oxide to affect the reflected shock velocity. Hence, the difference between the theoretical and observed velocities must be attributed either to the finite vibrational relaxation time or to a consistent error in the measurement of the reflected shock velocity.

The effect of a finite vibrational relaxation time was investigated by calculating the reflected shock velocity for a calorically perfect gas (constant C_p). Calculations were performed assuming C_p = 11 and 7 cal/mole °K which correspond to values representing two fully excited vibrational modes and no vibrational relaxation, respectively. In equilibrium, nitrous oxide has a specific heat of 11 cal/mole °K at 500°K. The results of these calculations are shown in Figure 6. As observed from this figure the calculations based on the assumption of no vibrational excitation fit the apparent reflected shock velocities quite well. In view of the fact that the vibrational relaxation time in the doubly degenerate mode is less than one microsecond, there must exist another cause for the observed discrepancy between the calculated and observed reflected shock velocities.

According to Mark (Ref. 17), the reflected shock wave interacts with the incident gas boundary layer to form a complex shock configuration, called a bifurcation, near the walls of the tube. This complex shock configuration is a result of the reflected shock wave moving at a greater velocity into the boundary layer, which has a lower stagnation pressure than the "free stream" incident gas. Essentially, the area of interaction, called the "foot," precedes the reflected shock by an amount dependent on the incident Mach number and the ratio of specific heats. The distance that the foot precedes the shock increases with a decrease in the ratio of specific heats. For noble gases this distance is very small and cannot be observed with a schlieren trace. However, with more complex molecules which have a lower ratio of specific heats, this distance can be appreciable. High-speed photographs of the reflected shock wave in nitrous oxide were obtained by Strehlow, et al., (Ref. 15) and they show that this distance is quite large. As a result of the bifurcation the reflected shock wave accelerates until eventually a steady-state distance is maintained between the reflected shock and the leading edge of the foot. Initially, however, the foot is traveling at a greater speed than the reflected shock wave. Thus a velocity measurement of what, at first, appears to be the reflected shock wave is actually the velocity of the foot. Figure 7 is a trace which shows both the foot and the reflected shock. The reflected shock wave appears as a dark region behind the foot and is seen to accelerate.

In this particular experiment the temperature behind the reflected shock wave was too low for the reaction to proceed sufficiently fast to produce this acceleration. Hence the attempt to obtain the rate of decomposition of nitrous oxide by the measurement of the reflected shock acceleration was unsuccessful.

Measurements of the initial velocity of the reflected shock wave are shown in Figure 6 as squares. It can be seen that they cluster about the curve based on a specific heat which included the doubly degenerate vibrational mode, $C_p = 11$ cal/mole ^{o}K. Hence the agreement between the predicted and actual reflected shock velocities is very good for incident shock velocities below 1200 m/sec. The radiation behind the reflected shock wave precluded any attempt to correct the measurement of the reflected shock velocity for the three data points obtained at incident shock velocities greater than 1500 m/sec. However, considering the magnitude of these measured reflected shock velocities and the intense radiation, it can be concluded that the nitrous oxide decomposed sufficiently rapid to affect the velocity of the reflected shock wave. A careful study of the two strongest incident shock waves reveals that the intense radiation commences immediately after passage of the reflected shock wave.

CONCLUSIONS

In conclusion it can be stated that the nitrous oxide decomposes instantly when the temperature and pressure are higher than 2400^{o}K and 36 atmospheres respectively. In the temperature region below 2400^{o}K the decomposition appears to have an induction period which is probably due to the finite relaxation time of the lower valence mode.

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APPENDIX I

CALCULATION OF ENTHALPY OF NITROUS OXIDE

For the calculation of the conditions behind shock waves it is necessary to know the enthalpy of the various constituents appearing in the gas mixture. In the decomposition of nitrous oxide the following species play an important role: N_2O, N_2, O, O_2, and NO. It is not necessary to include atomic nitrogen since, at temperatures below 3000°K, the equilibrium concentration of N is very small. The enthalpies of the four basic components can be found in any table of thermodynamic properties of gases. However, values of the enthalpy of nitrous oxide are given up to a maximum temperature of 1500°K only based on data published by Pennington and Kobe (Ref. 3).

The method used by Pennington includes the effect of stretching of the intermolecular bonds and the anharmonicity in the vibrational potential both of which increase with temperature. These calculations are very cumbersome and require an electronic computer, which could not be made available for this work. The classical method provides adequate results at reasonably low temperatures, depending on the gas, but the deviation from the correct value increases with temperature and at fairly high temperatures this deviation cannot be neglected. A graph showing the per cent deviation in enthalpy is given in Figure 8 for CO_2 and H_2O. Since CO_2 and N_2O are both linear tri-atomic molecules, it can be assumed that the type of correction to be made to the classical method should, to a first approximation, be the same. It is assumed that the slope (deviation per degree Kelvin) of the correction curve for both gases is the same. The per cent corrections for carbon dioxide vary linearly with temperature as follows:

$$\text{Per cent deviation} = AT - B$$

where

$$A = 6.36 \times 10^{-4}\ \%/^{\circ}K$$

$$B = 0.620\%$$

Thus for N_2O it is only necessary to determine the value of the constant B. In order to determine this constant the classical value of the enthalpy of N_2O was calculated for a temperature of 1500°K and compared with the corrected value from Reference 10. Since the electronic energy levels of N_2O are too high to contribute to the enthalpy at temperatures below 3000°K, the enthalpy was calculated by means of the following equation

$$H_T - H_{295} = 3.5T + \frac{2(850)}{\exp\left(\frac{850}{T}\right) - 1} + \frac{1840}{\exp\left(\frac{1840}{T}\right) - 1} + \frac{3200}{\exp\left(\frac{3200}{T}\right) - 1} - 1137$$

which includes only translation, rotation, and vibration.

The characteristic vibrational temperatures

$$\Theta_{vib}^{(1)} = \Theta_{vib}^{(2)} = 850^{\circ}K, \quad \Theta_{vib}^{(3)} = 1840^{\circ}K, \text{ and } \Theta_{vib}^{(4)} = 3200^{\circ}K$$

agree with those used by Pennington and Kobe. The differences between the data of Pennington and Kobe and those derived from the classical expression are listed in Table II. The estimated values of enthalpy differences, which include the approximate corrections for the deviation from the classical values, are listed in Table II also.

APPENDIX II

THE CALCULATION OF THERMODYNAMIC PROPERTIES BEHIND A REFLECTED NORMAL SHOCK WAVE

Calculation of these properties usually is given for gases with constant specific heats. Under conditions where the specific heats vary with temperature the calculations must be based on the actual enthalpies of the gases. Calculations based on constant specific heats apply to cases where the internal degrees of freedom of the molecules are completely frozen, whereas calculations involving the actual enthalpies represent the case where complete thermodynamic equilibrium prevails.

The equations for determining the thermodynamic properties of the shocked gas are most easily obtained when the coordinate system is moving with the velocity of the shock wave relative to the unshocked gas, u_1, (Fig. 9). The equations of continuity, momentum, and energy are written as follows:

$$\rho_1 u_1 = \rho_2 u_2 \tag{1}$$

$$p_1 + \rho_1 u_1^2 = p_2 + \rho_2 u_2^2 \tag{2}$$

$$h_1 + \frac{u_1^2}{2} = h_2 + \frac{u_2^2}{2} \tag{3}$$

Assuming that the perfect gas law can be used:

$$p_i = \rho_i \frac{\mathcal{R} T_i}{\mathfrak{M}_i} \tag{4}$$

From Eqs. (1) and (2), the shock wave velocity can be calculated.

$$u_1 = \sqrt{\frac{p_1}{\rho_1} \frac{p_2/p_1 - 1}{1 - \rho_1/\rho_2}} \tag{5}$$

Substituting Eqs. (5) and (1) into Eq. (3), the Hugoniot equation is obtained

$$(h_2 - h_1) = \frac{1}{2}\frac{p_1}{\rho_1}\left(\frac{p_2}{p_1} - 1\right)\left(\frac{\rho_1}{\rho_2} + 1\right) \tag{6}$$

from which the static pressure ratio across the shock wave can be calculated easily when it is assumed that no chemical reactions occur because in that case $\mathcal{M}_1 = \mathcal{M}_2 = \mathcal{M}$ and $h_2 - h_1$ is independent of pressure. Thus

$$\frac{p_2}{p_1} = \frac{T_2}{T_1}\left\{\left(\frac{H-E_o}{\mathcal{R}T}\right)_{T_2} - \frac{1}{2}\right\} - \left\{\left(\frac{H-E_o}{\mathcal{R}T}\right)_{T_1} - \frac{1}{2}\right\}$$

$$+\sqrt{\left[\frac{T_2}{T_1}\left\{\left(\frac{H-E_o}{\mathcal{R}T}\right)_{T_2} - \frac{1}{2}\right\} - \left\{\left(\frac{H-E_o}{\mathcal{R}T}\right)_{T_1} - \frac{1}{2}\right\}\right]^2 + \frac{T_2}{T_1}} \tag{7}$$

The particle velocity can be obtained using Eq. (5) and Eq. (1)

$$u_1 - u_2 = \sqrt{\frac{\mathcal{R}T_1}{\mathcal{M}}\left(\frac{p_2}{p_1} - 1\right)\left(1 - \frac{T_2}{T_1}\frac{p_1}{p_2}\right)} \tag{8}$$

To calculate the properties behind the reflected shock wave and its velocity, u_r, the continuity, momentum and energy equations are used as follows

$$\rho_2\left[u_r + (u_1 - u_2)\right] = \rho_r u_r \tag{9}$$

$$p_2 + \rho_2\left[u_r + (u_1 - u_2)\right]^2 = p_r + \rho_r u_r^2 \tag{10}$$

$$h_2 + \frac{\left[u_r + (u_1 - u_2)\right]^2}{2} = h_r + \frac{u_r^2}{2} \tag{11}$$

The pressure ratio across the reflected shock wave is calculated from Eq. (11) upon elimination of the velocities by means of Eqs. (9) and (10)

$$\frac{p_r}{p_2} = \frac{T_r}{T_2}\left\{\left(\frac{H-E_o}{\mathcal{R}T}\right)_{T_r} - \frac{1}{2}\right\} - \left\{\left(\frac{H-E_o}{\mathcal{R}T}\right)_{T_2} - \frac{1}{2}\right\} + \sqrt{\left[\frac{T_r}{T_2}\left\{\left(\frac{H-E_o}{\mathcal{R}T}\right)_{T_r} - \frac{1}{2}\right\} - \left\{\left(\frac{H-E_o}{\mathcal{R}T}\right)_{T_2} - \frac{1}{2}\right\}\right]^2 + \frac{T_r}{T_2}} \qquad (12)$$

However, T_r/T_2 cannot be selected arbitrarily. It is determined by a second relationship between the pressure ratio, p_r/p_2, and the temperature ratio, $\frac{T_r}{T_2}$, across the reflected shock wave. This expression is obtained from Eqs. (9) and (10) upon elimination of the reflected shock wave velocity. From Eq. (9), the velocity of the reflected shock wave is

$$u_r = \frac{u_1 - u_2}{\frac{p_r}{p_2}\cdot\frac{T_2}{T_r} - 1} \qquad (13)$$

Elimination of $u_r + (u_1 - u_2)$ from Eq. (10) by means of Eq. (9) also yields the reflected shock wave velocity

$$u_r = \sqrt{\frac{\mathcal{R}T_2}{\mathcal{M}}\cdot\frac{\frac{p_r}{p_2} - 1}{1 - \frac{p_2}{p_r}\cdot\frac{T_r}{T_2}}} \qquad (14)$$

Equating Eqs. (13) and (14) results in the pressure ratio

$$\frac{p_r}{p_2} = \frac{1}{2}\left[\frac{T_r}{T_2} + 1 + \frac{(u_1 - u_2)^2}{\frac{\mathcal{R}T_2}{\mathcal{M}}}\right] + \sqrt{\frac{1}{4}\left[\frac{T_r}{T_2} + 1 + \frac{(u_1 - u_2)^2}{\frac{\mathcal{R}T_2}{\mathcal{M}}}\right]^2 - \frac{T_r}{T_2}} \qquad (15)\ ,$$

where according to Eq. (8)

$$\frac{(u_1 - u_2)^2}{\dfrac{\mathcal{R} T_2}{\mathfrak{M}}} = \frac{\left(\dfrac{p_2}{p_1} - 1\right)\left(\dfrac{p_2}{p_1} - \dfrac{T_2}{T_1}\right)}{\dfrac{p_2}{p_1} \cdot \dfrac{T_2}{T_1}} \qquad (16)$$

With these equations the procedure for calculating the parameters of the reflected shock wave is as follows. For given values of the initial gas temperature, T_1, and its molecular mass, $\mathfrak{M}$, the pressure ratio, $\frac{p_2}{p_1}$, across the incident shock wave is calculated for certain arbitrarily assumed values of the temperature T_2 behind the incident shock wave by means of Eq. (7). The values of the reduced enthalpy, $\left(\frac{H-E_0}{\mathcal{R} T}\right)_T$, are taken either from a graph or a table. The incident shock wave velocity is calculated from Eq. (5) and the particle velocity, $u_1 - u_2$, from Eq. (8). Then the pressure ratio, $\frac{p_r}{p_2}$, across the reflected wave is calculated by trial and error by solving Eqs. (12) and (15) simultaneously with arbitrarily assumed temperature ratios $\frac{T_r}{T_2}$ until that value of $\frac{T_r}{T_2}$ has been found which gives the same values for $\frac{p_r}{p_2}$ from both equations. With these values of $\frac{p_r}{p_2}$ and $\frac{T_r}{T_2}$, finally, the reflected shock wave velocity is calculated from Eq. (13). Much more complex calculations are required when chemical changes occur because the molecular mass and the enthalpy difference $h_2 - h_1$ and $h_r - h_2$ then depend on pressure. Graphs of T_2, p_2/p_1, T_r, and p_r/p_1 are given as functions of u_1 in Figures 10, 11, and 12. Since the temperature of the initial gas is always about 295°K, this value was chosen as the initial temperature, T_1.

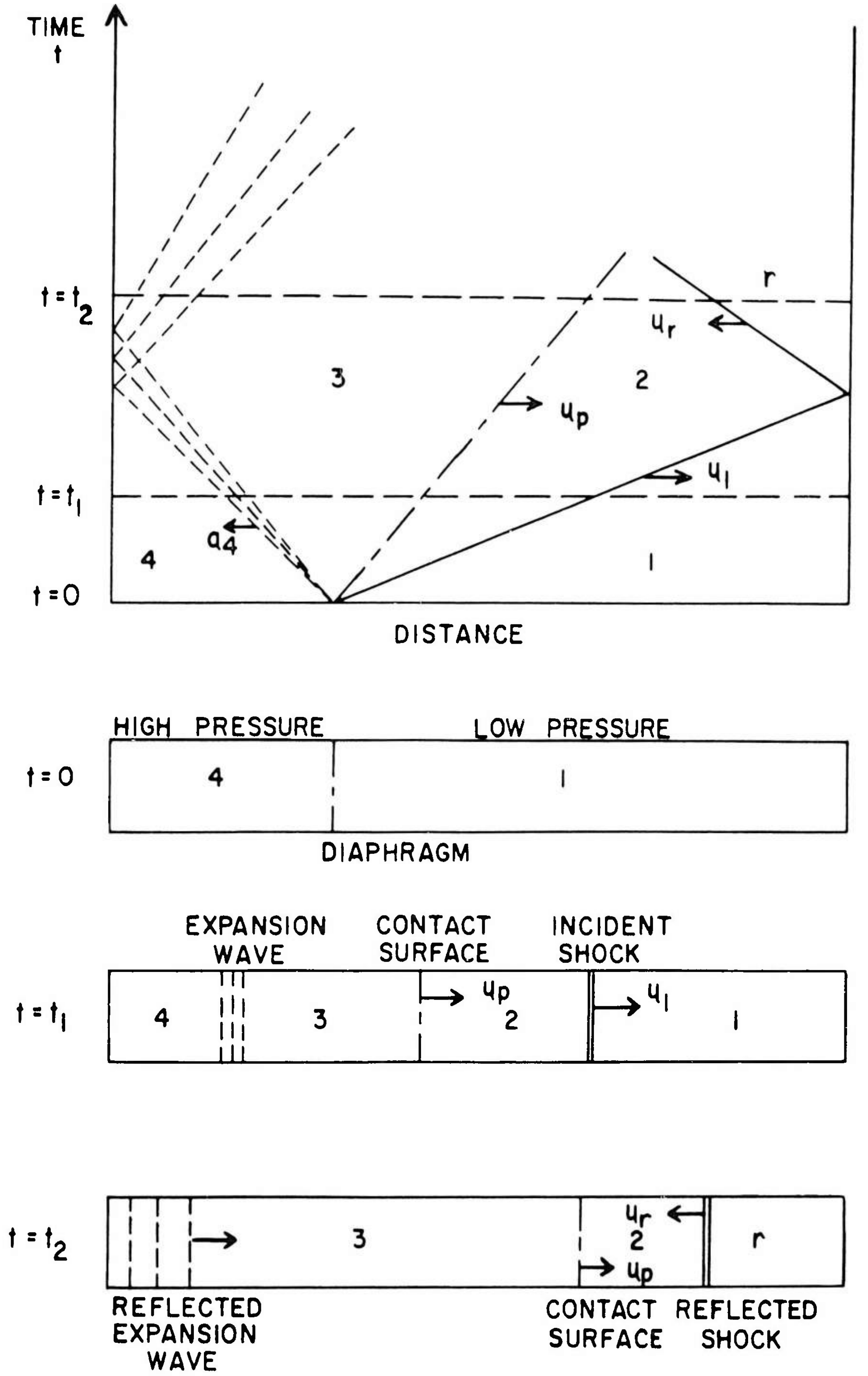


FIG. 1 WAVE DIAGRAM OF SIMPLE SHOCK TUBE FLOW

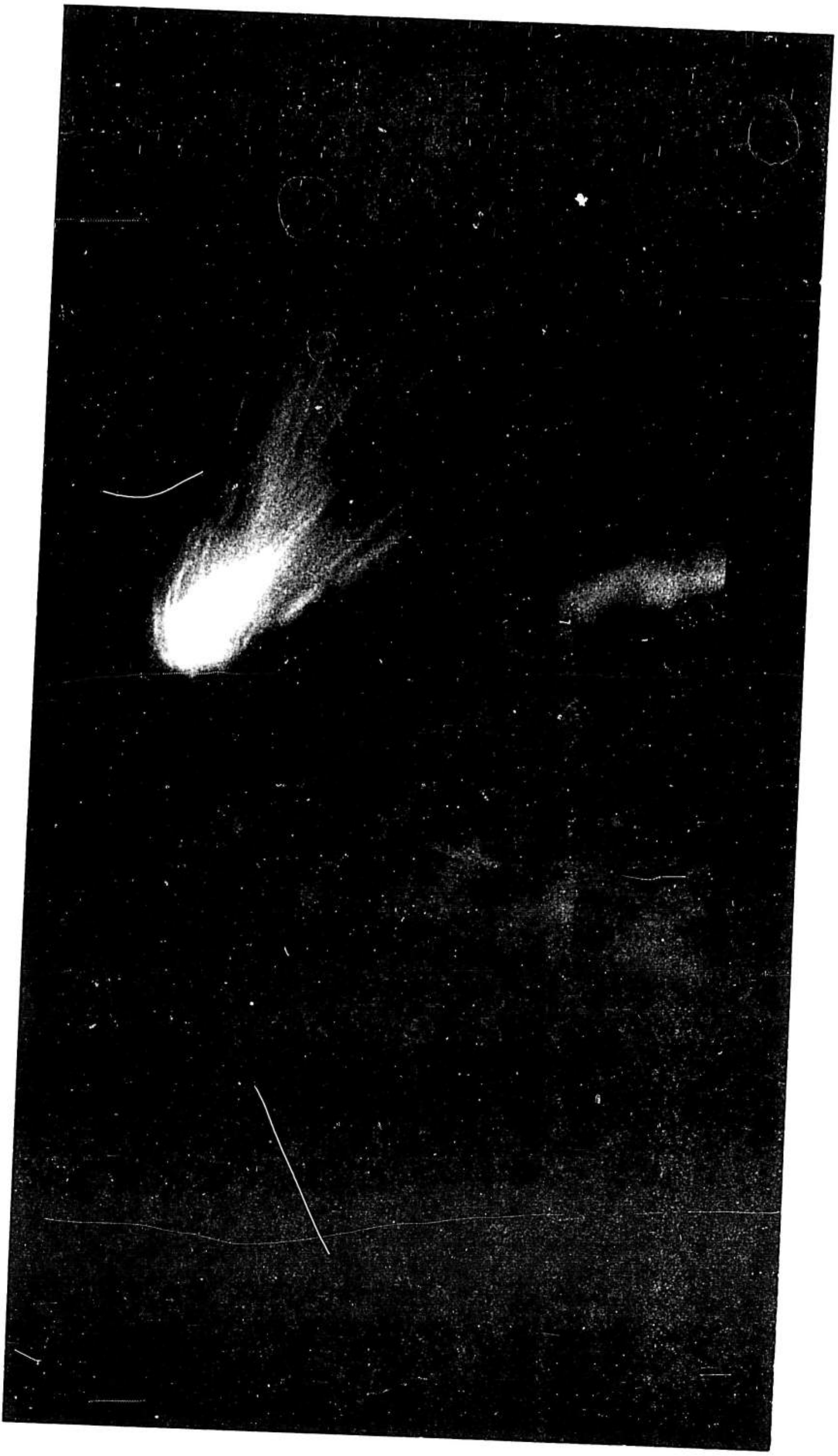


FIG. 2 WAVE TRACE OF EXPERIMENT 56

FIG. 3 WAVE TRACE OF EXPERIMENT 57

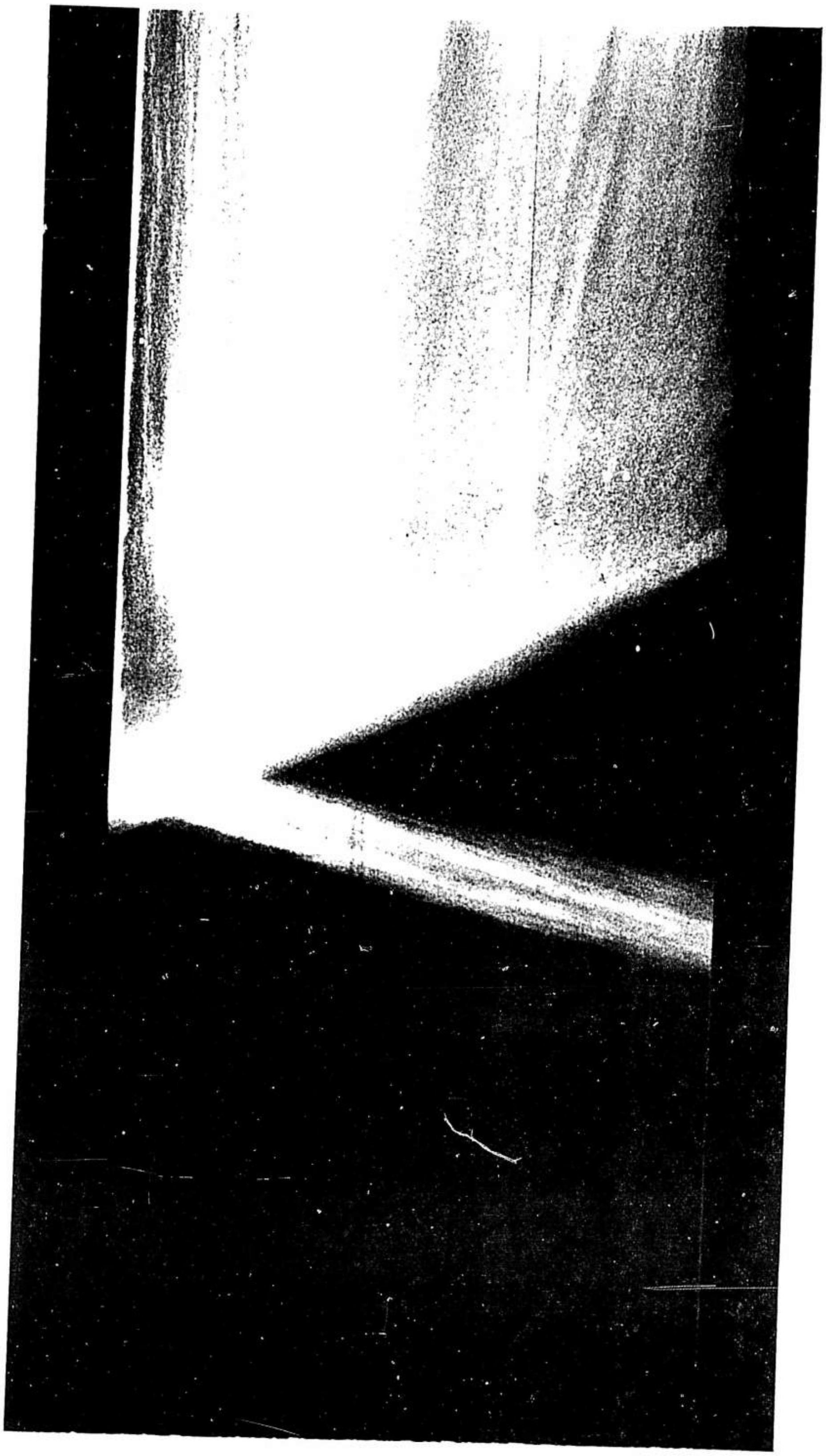


FIG. 4 WAVE TRACE OF EXPERIMENT 81

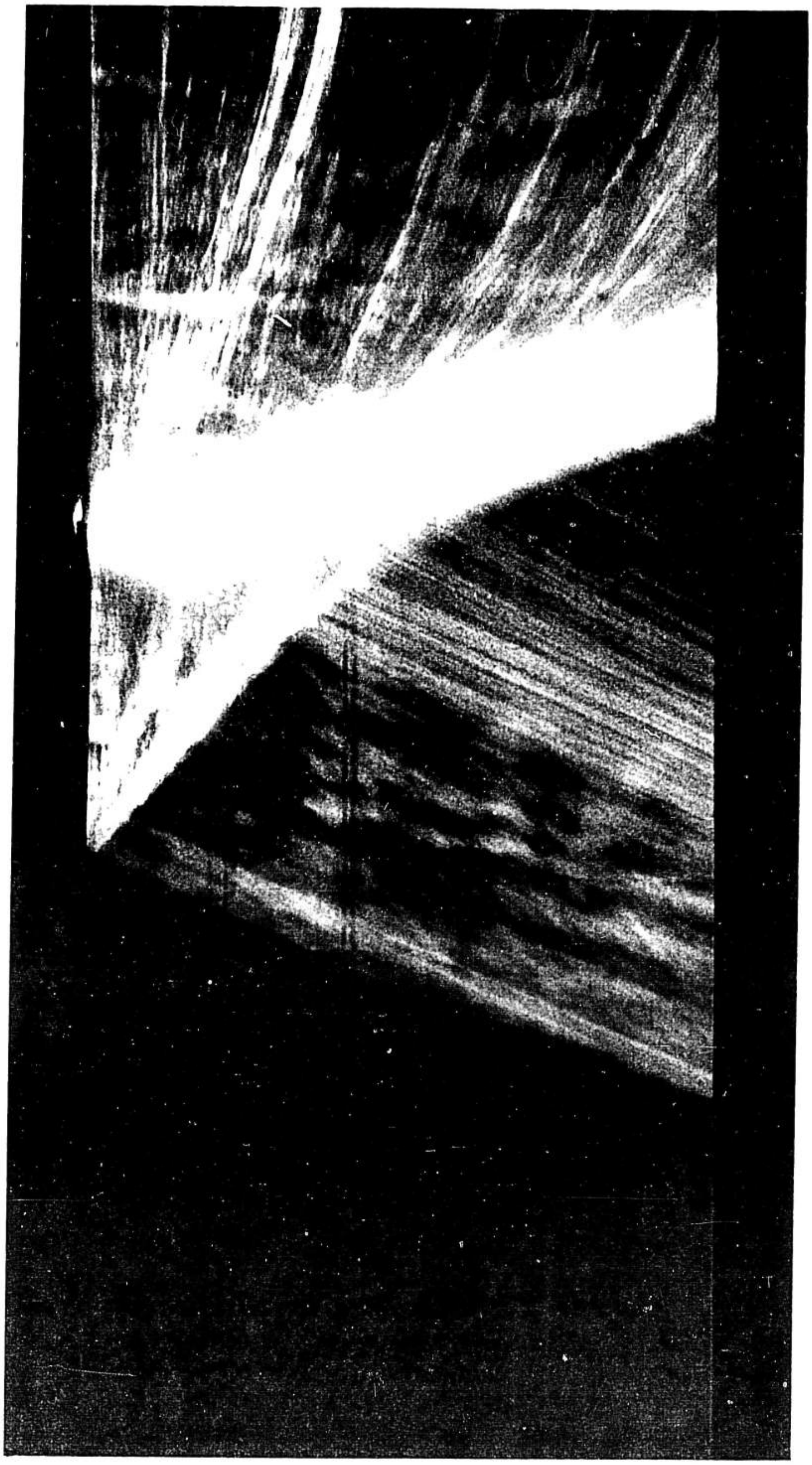


FIG. 5 WAVE TRACE OF EXPERIMENT 82

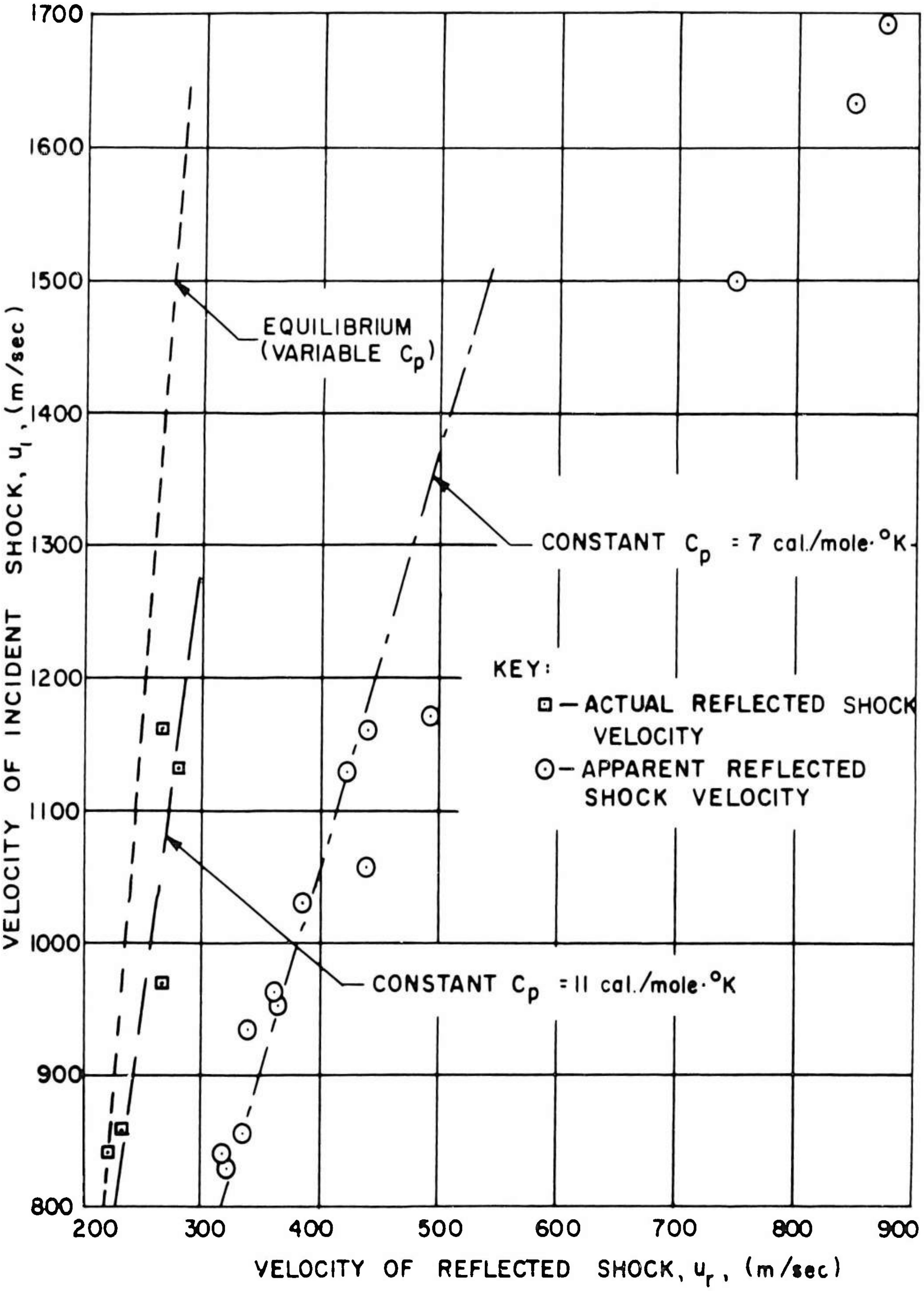


FIG. 6 CALCULATED AND MEASURED VALUES OF REFLECTED NORMAL SHOCK WAVE VELOCITIES AS FUNCTIONS OF THE INCIDENT NORMAL SHOCK WAVE VELOCITY

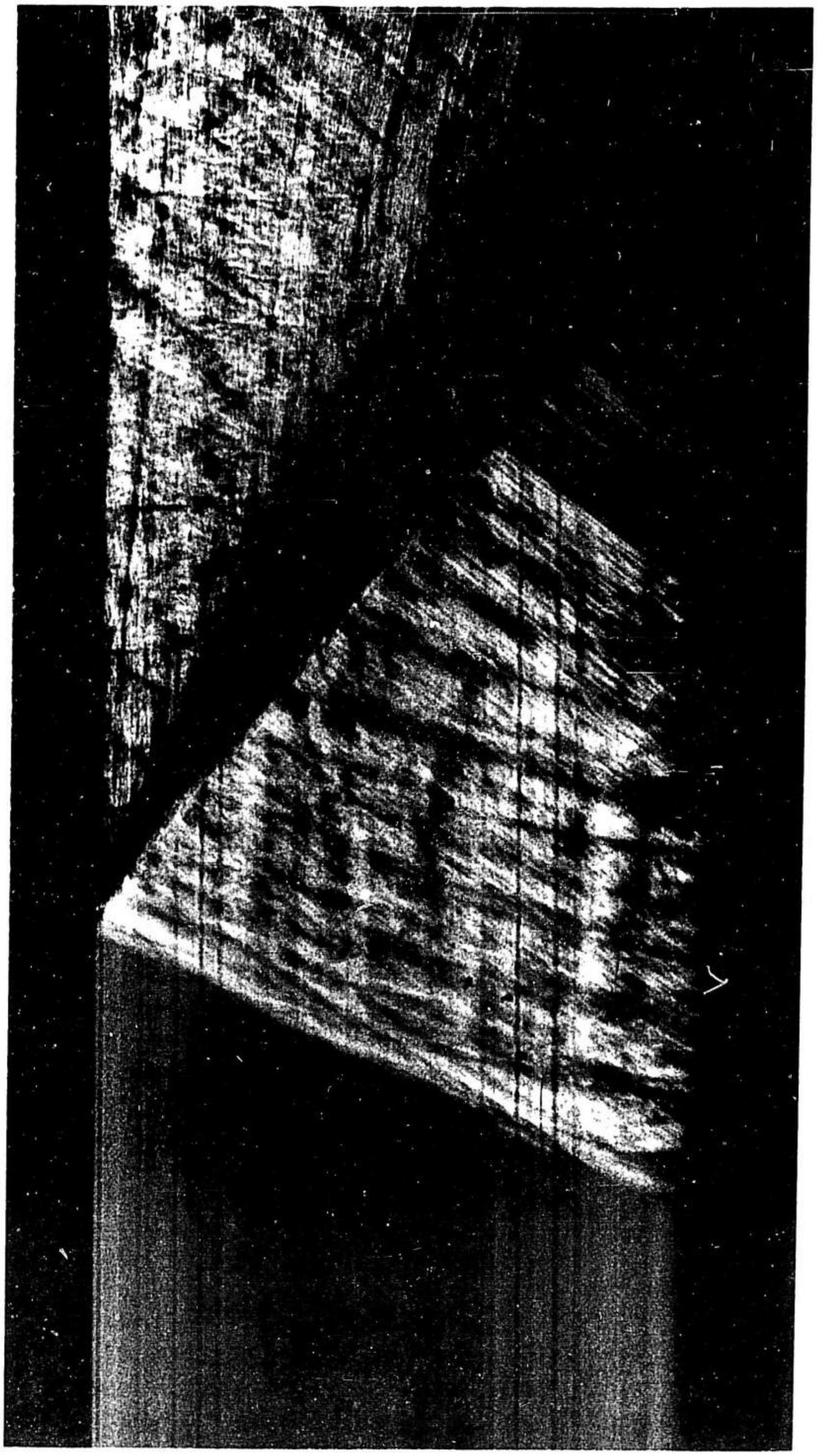


FIG. 7 WAVE TRACE OF EXPERIMENT 49

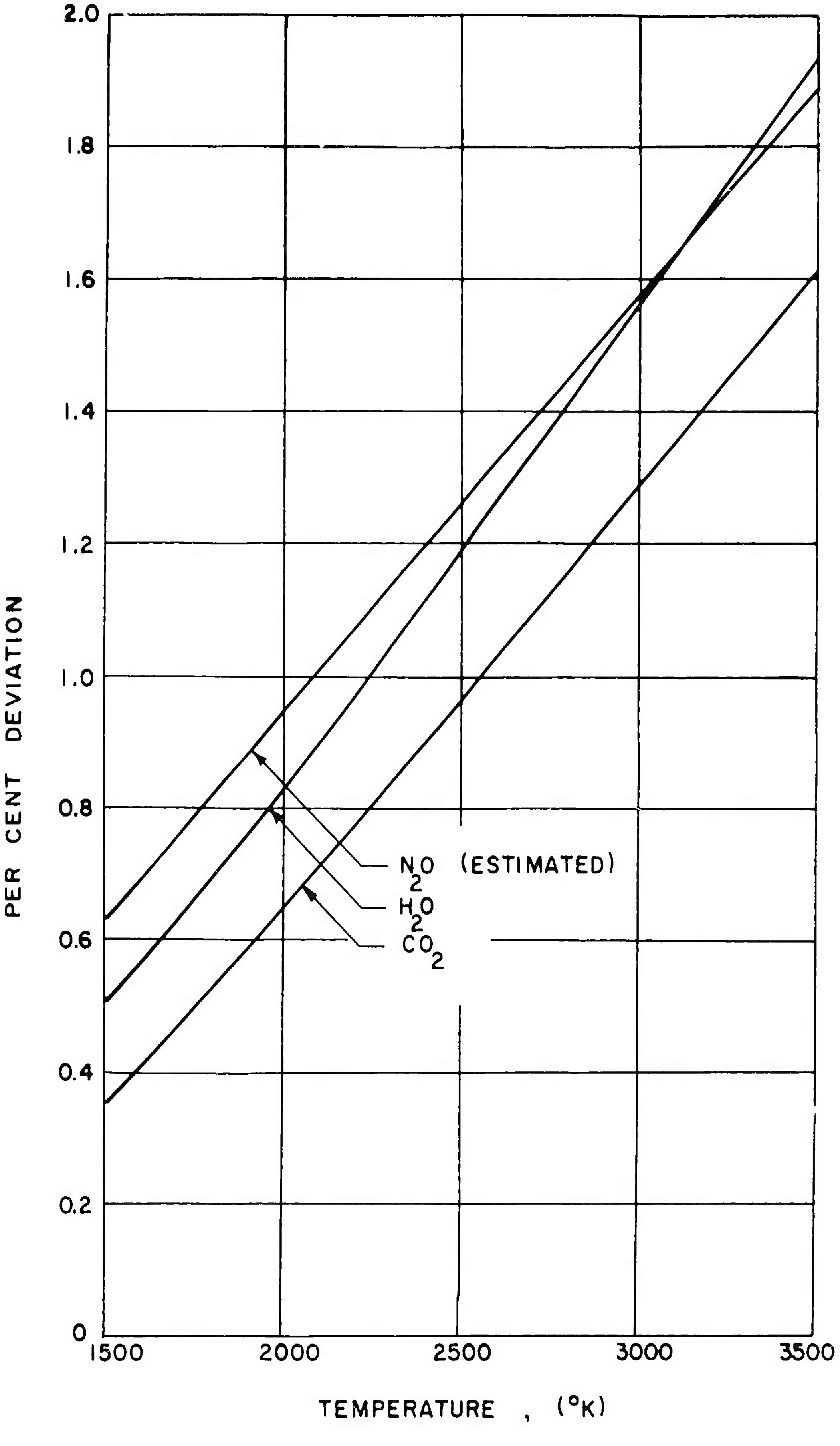
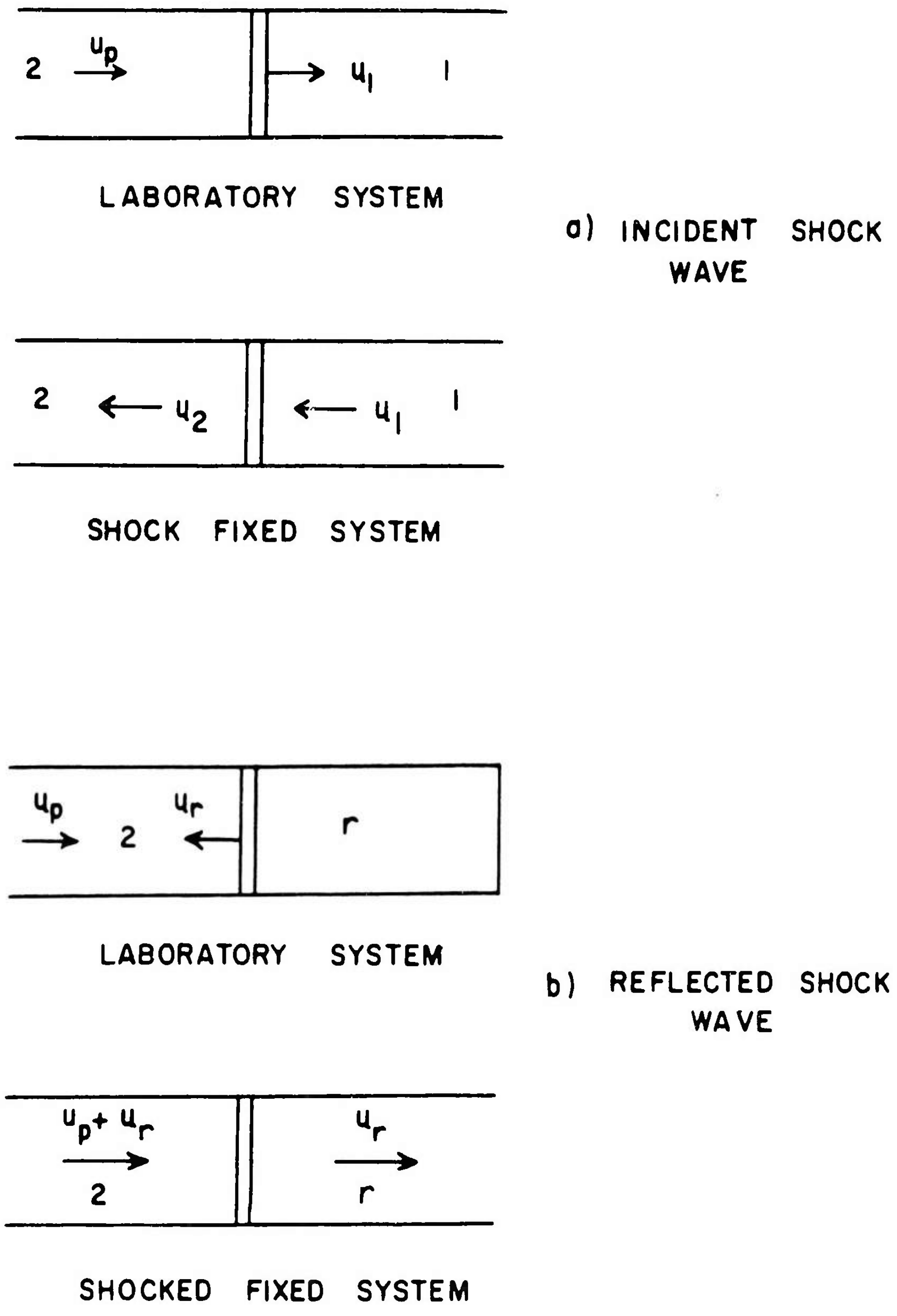


FIG. 8 EFFECT OF ANHARMONICITY AND STRETCHING ON THE ENTHALPIES OF CO_2 AND H_2O IN PER CENT OF CLASSICALLY CALCULATED VALUES



a) INCIDENT SHOCK WAVE

b) REFLECTED SHOCK WAVE

FIG. 9 COORDINATE SYSTEMS FOR SHOCK WAVE CALCULATIONS

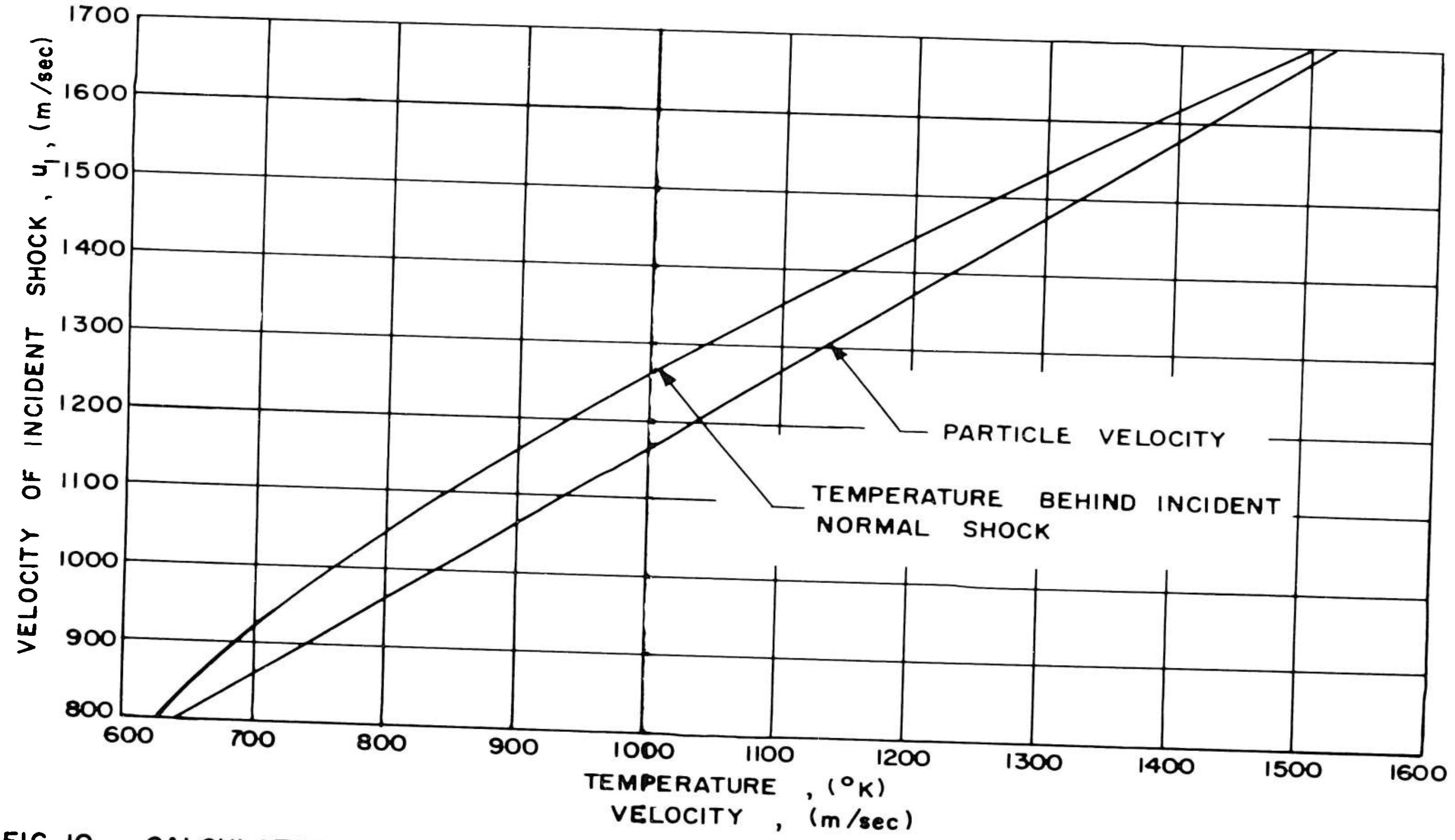


FIG. 10 CALCULATED PARTICLE VELOCITY AND TEMPERATURE BEHIND INCIDENT NORMAL SHOCK IN NITROUS OXIDE AS A FUNCTION OF THE NORMAL SHOCK VELOCITY

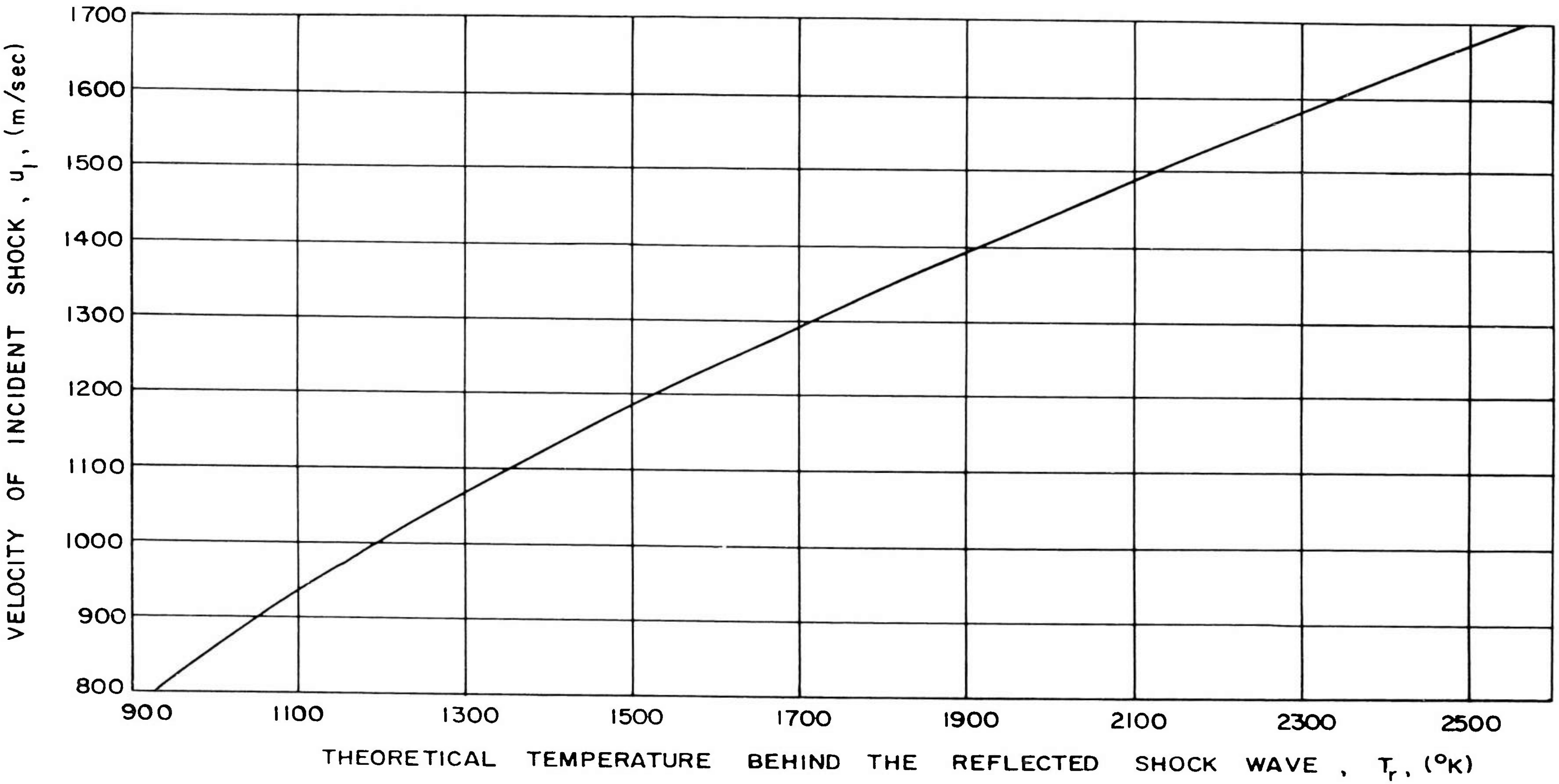


FIG. 11 CALCULATED TEMPERATURE BEHIND REFLECTED NORMAL SHOCK IN NITROUS OXIDE AS A FUNCTION OF THE INCIDENT NORMAL SHOCK VELOCITY

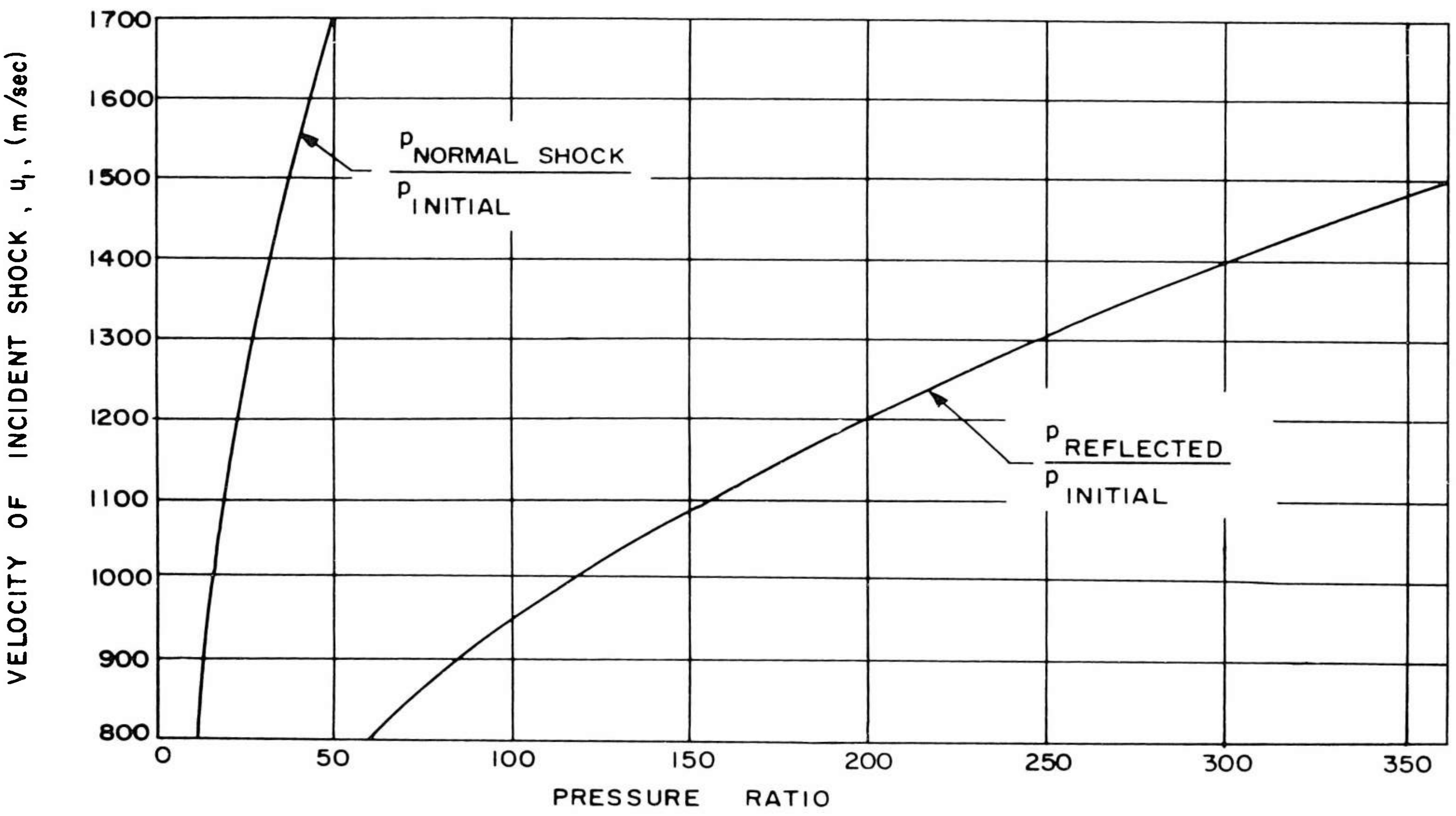


FIG.12 CALCULATED STATIC PRESSURE RATIOS ACROSS INCIDENT AND REFLECTED SHOCK WAVES IN NITROUS OXIDE AS A FUNCTION OF THE INCIDENT NORMAL SHOCK VELOCITY

TABLE I

EXPERIMENTAL RESULTS

Experiment	Initial Pressure (atm)	Incident Shock Wave Velocity (m/sec)	Equilibrium Conditions Behind Reflected Shock		Induction Time (Micro-Seconds)	Comments
			Pressure (atm)	Temperature (°K)		
29	1	761 ± 15	52	885	---	1
31	1	732 ± 15	48	840	---	1
32	1	1020 ± 20	123	1220	---	1
37	1	779 ± 10	55	900	---	1
38	1	788 ± 10	57	915	---	1
39	1	866 ± 10	75	995	---	1
41	1	965 ± 20	103	1150	---	1
44	1	1070 ± 10	142	1320	---	2
46	1	946 ± 10	98	1110	---	1
49	1	840 ± 10	68	970	---	1
50	1	870 ± 10	76	1010	---	1
51	1	858 ± 10	73	995	---	1
52	1	924 ± 10	91	1085	---	1
53	1	833 ± 18	66	960	---	1
54	1	964 ± 10	104	1145	---	1
56	1	1131 ± 15	167	1430	152	3
57	0.099	1500 ± 30	36	2120	55	3
67	0.11	1173 ± 25	20.4	1505	---	2
71	0.14	1055 ± 10	19.4	1290	---	1
72	0.20	1030 ± 10	25.4	1240	---	1
73	[illegible]	952 ± 10	26.3	1120	---	1

TABLE I (Cont'd)

EXPERIMENTAL RESULTS

Experiment	Initial Pressure (atm)	Incident Shock Wave Velocity (m/sec)	Equilibrium Conditions Behind Reflected Shock		Induction Time (Micro-Seconds)	Comments
			Pressure (atm)	Temperature (^{o}K)		
81	0.079	1695 ± 20	39.5	2510	---	3
82	0.20	1160 ± 12	35.0	1480	150	3
83	0.31	936 ± 10	29.5	1100	---	1
84	0.079	1635 ± 17	36.2	2400	---	3
85	0.079	910 ± 20	6.9	1060	---	1
89	0.079	850 ± 18	5.6	980	---	1
90	0.083	1110 ± 20	13.1	1395	---	1

Comments.
1. No rapid decomposition behind reflected shock wave.
2. Luminescent glow behind incident and reflected shock wave attributed to trace of carbon in the tube.
3. Apparent decomposition, see Section IV, experimental results.

TABLE II

RELATIVE ENTHALPY OF NITROUS OXIDE, $H_T - H_{295}$

Temperature, T (^oK)	Classical (cal/mole)	Pennington and Kobe (cal/mole)	Estimated (cal/mole)
500		2075	
600		3204	
700		4390	
800		5623	
900		6896	
1000		8202	
1100		9535	
1200		10891	
1300		12248	
1400		13662	
1500	14974	15069	
1600	16371		16485
1700	17780		17915
1800	19196		19353
1900	20626		20809
2000	22051		22260
2100	23489		23726
2200	24930		25198
2300	26377		26672
2400	27826		28160
2500	29268		29638
2600	30722		31131
2700	32185		32622
2800	33637		34127
2900	35095		35628
3000	36547		37126

Aeronautical Research Laboratories. Wright-PAtterson AFB. Ohio CHEMICAL KINETICS OF NITROUS OXIDE DECOMPOSITION AT ELEVATED PRESSURES AND TEMPERATURES by E. Stokes Fishburne, Rudolph Edse, Ohio State University Rocket Research Laboratory, Columbus, O. September 1962. 31 p. incl. illus. tables. (Prpject 7065. Task 7065-01) (Contract AF 33(616)-5615) (ARL 62-430) Unclassified Report

Kinetic studies of the thermal decomposition of nitrous oxide were conducted in the temperature range from 1000 to 2500°K. The decomposition of nitrous oxide behind

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the reflected shock wave in a shock tube was investigated using photographic techniques. It appears that the rate of decomposition may be governed by the vibrational relaxation time of the lower energy valence bond. Induction times for the rapid decomposition of nitrous oxide range from 152 microseconds at 1430°K agrees qualitatively with approximate values obtained by other investigators.

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