DETONATION AND SHOCK-TUBE STUDIES OF HYDRAZINE AND NITROUS OXIDE

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GOTTINGEN, GERMANY

SEPTEMBER 1963

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Contract AF 61(514)-1142
Project 7013
Task 7013-01

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WRIGHT-PATTERSON AIR FORCE BASE, OHIO
FOREWORD

This report was prepared for the Aerospace Research Laboratories of the Office of Aerospace Research at Wright-Patterson Air Force Base, Ohio, by the Institute of Physical Chemistry at the University of Göttingen in Germany under Air Force Contract No. AF 61(514)-1142, Project No. 7013, "Research in Chemical Energetics", Task No. 70130. "Research on Energetic Processes in Gases". The project director at the University of Göttingen was Professor W. Jost, Head of the Institute of Physical Chemistry. Karl Scheller served as technical administrator for the Aerospace Research Laboratories. The report reviews the research performed during the period 1 March 1962 - 28 February 1963.
ABSTRACT

In continuing studies of kinetic and detonative properties of simple compounds, which contain nitrogen, experiments investigating the detonability of hydrazine-nitrous oxide mixtures are reported. No detonations could be produced in mixtures containing less than 7 vol.% of N₂O. Pure hydrazine shows a detonation velocity of about 2450 m/sec, which is close to the theoretical value calculated on the assumption of chemical equilibrium in the CHAPMAN-JOUGUET region. The measured velocities meet some of the criteria for stable detonations.

Spectroscopic investigations of the wake behind N₂H₄ detonations, however, revealed great amounts of ammonia which had not yet disappeared 300 μsec behind the detonation front. Such quantities of NH₃ and this long a reaction zone is not in accord with the measured velocity of the detonation. Some evidence based on the pressure dependence in the NH₃ production suggests that these detonations are inherently unstable.

In compiling data for the understanding of the kinetic aspects of the above detonations, shock-tube studies of the pyrolysis of nitrous oxide and hydrazine have been continued. Absorption coefficients of N₂ up to 1800 K have been measured. In the temperature interval from 1530 K to 1820 K and at total gas densities of 1.5·10⁻⁴ mole/cm³ (6 atm.) the initial decomposition rate of N₂O mixed with an excess of Ar is given by the rate law \( k_1 = 10^{10.8} \exp(-60 000/RT) \text{ sec}^{-1} \). This is in agreement with results from measurements of the unimolecular decomposition rate at low temperatures. The second-order dependence of \( k_1 \) upon total
Gas density suggests that this unimolecular reaction is determined by collisional activation under the present conditions. Photoelectric techniques are outlined which will allow the amount of nitric oxide formed in this reaction to be determined. Registration of the emission indicated the presence of the reaction
\[ \text{NO} + \text{O} \rightarrow \text{NO}_2^+ \rightarrow \text{NO}_2 + \text{hv} , \]
even at the comparatively high pressures of these experiments.

Measurements of the decomposition rate of hydrazine behind reflected shock waves with an excess of He have been extended up to temperatures of 1550 °K. Using He as a carrier gas reduces schlieren effects and facilitates the kinetic evaluation of short reaction periods, even though the shock-front curvature has to be accounted for. Extinction coefficients behind the incident shock waves were in agreement with those obtained in previous experiments with Ar. By appropriate evaluation of the half-lives it was established, that the rate of decomposition does not depend upon the nature of the carrier gas. Contrary to the results obtained in the temperature region between 1100 °K and 1400 °K, there was no distinguishable dependence of half-lives of hydrazine upon its partial density. The apparent energy of activation is not different than in the low temperature region, i.e. 40 kcal/mole.

Limitations of the present shock tube are indicated and a new tube, which has been constructed to meet more stringent requirements, is described.
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SYMBOLS

$\Delta J$ (subscript) refers to Chapman-Jouguet state

$\Delta E$ energy of reaction

$D$ detonation velocity

$F$ (subscript) refers to parameters in the shock front of a detonation

$H$ enthalpy

$\Delta H_r$ enthalpy of reaction

$I$ recorded intensity of light

$I_0$ intensity of light without absorption in the gaseous phase

$i$ (subscript) refers to parameters at an intermediate stage of the reaction zone

$k$ rate constant of chemical reaction

$M$ Mach number

$P$ pressure

$R$ specific gas constant

$s$ slit width of monochromator

$T$ temperature

$t$ time

$t_r$ time interval between registration of detonation front and reflected shock wave

$u$ shock speed

$u/u_1$ attenuation of incident shock (per m)

$u_5/u_1$ velocity ratio of reflected and incident shock waves

$x$ geometric path length in absorption measurements

$\alpha$ parameter representing amount of $NH_3$ formed behind detonations through hydrazine

$\beta$ parameter representing amount of $NH_3$ which has survived for a certain period of time in the wake of.
\[ \gamma \] ratio of specific heats

\[ \varepsilon \] decadic molar extinction coefficient

\[ \lambda \] wavelength

\[ \varphi \] gas density

\[ \tau_{1/2} \] half-life of reacting molecules

\[ \mathcal{S} \] degree of reaction

superscript 1 refers to initial gas in front of shock waves and detonations

" 2 refers to gas behind shock waves

" 5 refers to gas behind reflected shock waves
A. Studies of Detonations of Hydrazin-Nitrous Oxide Mixtures.

I. INTRODUCTION

Within this general program, in which the reaction behavior of hydrazine at elevated temperatures is investigated in the homogeneous gas phase, the interaction of hydrazine with various oxidizers is of both practical and theoretical concern. Flames supported by mixtures of hydrazine with oxygen, nitric oxide and nitrous oxide have been studied extensively in recent years (ref. 1-4). Some detailed investigations on the explosive combustion of hydrazine (ref. 5) have revealed several features peculiar to the oxidation of hydrazine. Studies of the detonability and reaction zone of detonations through hydrazine-oxidizer mixtures are expected to add some information to previous results.

The detonability of pure gaseous hydrazine at atmospheric pressure had been examined before (ref. 6). At that time, difficulties were met in combining hydrazine and nitric oxide or oxygen to form gaseous mixtures which were well defined at a pressure of 1 atm. Furthermore, it was shown that nitrogen dioxide could not be added to hydrazine at room temperature without immediate reaction (ref. 7). Nitrous oxide, on the other hand, can be saturated with hydrazine readily and the mixture is easy to deal with at temperatures below 70 °C, thus offering a convenient approach to studies of detonative combustion of hydrazine.
II. EXPERIMENTAL

A round aluminum tube was chosen for these detonation experiments with \( \text{N}_2\text{H}_4\text{-H}_2\text{O} \) mixtures. The test section had a length of 300 cm and a diameter of 8.4 cm (fig. 1). Three observation windows made of plexiglass were inserted 10 cm apart, the last one being 11 cm upstream from the end plate. All windows were mounted flush with the inner wall so that the gas flow was not disturbed. The whole tube was surrounded by an electric tape and could be heated uniformly.

The temperature of the test section had to be chosen according to the desired partial pressure of hydrazine, this being contingent upon condensation phenomena (ref. 6,8). At higher temperatures, hydrazine undergoes catalytic decomposition when in contact with metal and glass surfaces (cf. review in ref. 7). This would give rise to great uncertainties about the actual composition of the detonating gas mixtures. Hence, it was decided to restrict these measurements to initial temperatures of 43 °C (except for detonations with pure hydrazine vapor and mixtures containing 83 vol% hydrazine, where the temperature was 67 °C), entailing a partial pressure of hydrazine of less than 40 mm Hg. Total pressures of the test mixtures lay, in general, around 90 mm Hg in the reported series of measurements.

Detonations of mixtures with 7-30 vol% hydrazine in nitrous oxide, as well as of pure hydrazine, were initiated by hydrogen-oxygen detonations in a driver section 160 cm long and with the same diameter as the test section. Initiator gas and test mixtures were separated by an aluminum foil which ruptured
under the impact of the initial detonations.

The pressure in the initiator section was made high enough (450 mm Hg, viz. 5 times higher than the initial pressure of the test gas, cf. ref. 9, p. 356) so that detonations of the nitrous oxide-hydrazine mixtures could be initiated readily. The composition of the initiator was conveniently set by restricting the flow rates of hydrogen and oxygen with the aid of properly gauged capillaries before the partners were mixed and passed through the driver section. Flow velocities were controlled by means of capillary flow meters. Two different mixtures of the initiator gas were used, the one contained 40 ± 2 vol% H₂ the other one 60 vol% H₂ (balance O₂), providing calculated detonation velocities of D=2080 ± m/sec and D=2770 m/sec. The former value lay in the range expected for detonation velocities of the test mixtures considered.

The test mixtures with 70 vol% N₂O or more were prepared by passing nitrous oxide, after expansion to a lower pressure, twice through liquid hydrazine (fig. 1). Difficulties in saturating gases with hydrazine vapor have been reported before (cf. 6 and 7). Even though hydrazine evaporates sluggishly, it condenses readily. Thus, when leading partially saturated N₂O through a condenser, the temperature of which was kept approximately 10 °C below that of the saturator, the partial pressure of hydrazine in the gas flow could be calculated reliably on the basis of the condenser temperature.

The glass tube transitioning the N₂O-N₂H₄ mixture to the test section, as well as the test section itself, were heated
appreciably above the condensation temperature of hydrazine. Still, previous experiments had shown (ref. 6 and 7) that adsorption of hydrazine at the tube wall might produce great deviations from the initial concentration of hydrazine. Therefore, the test section was swept a few times with the test mixture under the initial pressure of an experiment. The higher the partial pressure of hydrazine, the larger the amounts of gas were which had to be passed through the tube before the interfacial equilibrium was approached. In order to reach this point within a reasonable period of time, a special valve was constructed (see fig. 1 and fig. 21, p. 58) which allowed adequate flow velocities (ca. 10 cm³/sec STP and higher).

In general, the gas volume in the test section was replaced at least eight times before an experiment was started. Even though this method was suitable to gas mixtures containing lower concentrations of hydrazine, it quite evidently failed for mixtures with more than 30 % H₂H₄.

In preparing test gas mixtures with 30–100 vol.% H₂H₄, another principle was used (fig. 2). Liquid hydrazine stored at room temperature and 27 atm atmospheric pressure from a graduated 21 cm³, "litre," cylinder into a capillary which was heated to about 80 °C by a surrounding electric tape. Thus, the capillary served both as evaporator and flow regulator, viz. expansion nozzle down to a pressure of about 90 mm Hg. Beyond the capillary, the gaseous hydrazine could be mixed with nitrous oxide, which had been pro-

![Diagram](image-url)
heated while streaming through another capillary. The flow velocity of hydrazine was controlled by timing the outflow from the graduated cylinder and was shown to be reasonably constant (ca. 5 millimole/sec). The method proved to be reliable and without risk. Before, each run the test section was thoroughly evacuated in order to remove water which had been formed as a reaction product of the previous experiment.

Prior to measuring the initial pressure of the test gas by means of a mercury manometer, which was at room temperature, some nitrogen was administered to manometer $N_2$ (fig. 1), thus, providing a gas cushion and preventing the condensation of hydrazine. The composition of the test gas was not affected by this procedure, because the pressure was set during the flushing of the tube.

The initiator gas was ignited by slowly increasing the current through a filament (fig. 1), to avoid premature triggering of the oscilloscope. The speed was measured with the aid of a conventional schlieren arrangement; three photomultipliers (ROA 951a) converted the light signals to electric pulses; the first schlieren spike triggered the oscilloscope sweep (Tektronix 545, 53/54 II plug-in unit). The electric time constant was calculated to be ca. 6 μsec.

Fig 3
Fig. 3 shows a typical oscilloscope record. The positive pips are 100 μsec timing markers furnished by a Tektronix time-mark generator (Type 181, quartz-stabilized). The first schlieren-signal is clearly recorded on the screen. As the detonation front proceeds, greater and greater thermal radiation is recorded by the three photomultipliers and the photocurrent increases. The last abrupt change in photocurrent at the end of the trace is presumably caused by the strong light emission concomitant with the reflected shock. The detonation velocity could be measured with an accuracy of 0.5 %, after photographic enlargement of the oscilloscope records.

III. MATERIALS

Liquid anhydrous hydrazine, furnished by FLUKA AG, was employed without further purification. It contained less than 2 % water. Mass spectroscopic analysis indicated that the impurity level after evaporation was reduced to less than 0.1 %.

Nitrous oxide, anaesthetic grade, was provided by FARBEVERE HOSCHST AG and was at least 93 % pure. Since these experiments were of exploratory nature, further purification by distillation was not mandatory.

The leak rate of the test section amounted to $10^{-3}$ mm Hg/min. Most of the air passed into the range holding the diaphragm. In any case, it was computed that the test gas could not contain more than 0.1 % air due to leaking.
Detonation velocities did not show any attenuation or acceleration within the range of accuracy of these experiments. Depending upon the composition of the mixture, they ranged from 1803 m/sec (7.7 vol% \( N_2H_4 \)) to 2600 m/sec (83 vol% \( N_2H_4 \)) at initial pressures of \( P_1 = 90 \) mm Hg and \( P_1 = 63 \) mm Hg (fig. 4). The initial temperature was 316 °K except for experiments with 83 and 100 vol% \( N_2H_4 \). Then the initial temperature had to be raised to \( T_1 = 340 \) °K in order to provide a sufficient high vapor pressure. A mixture of nitrous oxide with 7.7 vol% \( N_2H_4 \) still produced detonations.

For mixtures containing 7 vol% and 6 vol% \( N_2O \) as well as for pure nitrous oxide, however, only strongly attenuated shock waves were recorded. With pure nitrous oxide, these shock velocities averaged around 930 m/sec for initiator mixtures of \( O_2+2H_2 \) and around 1210 m/sec for stoichiometric initiator mixtures \( (O_2+2H_2) \).

Detonation velocities of mixtures containing more than 7 vol% \( N_2O \) were faster by at least a factor of 2 than the above shock speeds. Within the accuracy of these determinations they did not show any attenuation or any dependence upon starting pressure \( (P_1 = 63 \text{ and } 90 \text{ mm Hg}) \) or composition of the initiator mixture. Nevertheless, strong fluctuations occur among the measured points (fig. 4). This might be due to inaccuracies in the test.
gas composition. The effects of adsorption of hydrazine on the walls and heterogeneous decomposition have not been investigated in these experiments. In any case, the points indicate a definite trend in the concentration and show some of the characteristics of stable detonations. The behavior of pure nitrous oxide sufficiently demonstrates that the measured velocities do not result from overdriven detonations. The limits of detonability have not been established exactly, because the present detonation tube does not fulfil the requirements of such determinations (ref. 9, p. 338).

In some experiments, where the time constant of the electrical recording unit was properly selected, the rise time of the schlieren signals was found to be as long as 5 μsec. (this is in agreement with the rise time of absorption signals, see p. 16).

The experimental arrangement (width of light beam) does not account for more than 0.5 μsec. Thus, one might conclude that the detonation front is either strongly curved or tilted, a phenomenon which usually appears in detonation waves of inherent instability (cf. e.g. ref. 16).

V. CALCULATION OF DETONATION VELOCITIES

The theoretical values for detonation velocities have been calculated by iteration under the assumption discussed in the literature (cf. e.g./9). Enthalpies of reaction and specific heat data have been taken from ref. 10, energies for the various components were obtained from ref. 11. The following table shows the results of the computation for six different mixtures at starting pressures of 90 mm Hg, including the equilibrium.
Fig. 4. Detonation Velocities of Nitrous Oxide - Hydrazine Mixtures
concentrations of the species NO, OH and O in the Chapman-Jouguet zone. Subscript F refers to conditions just behind the shock front, subscript C-J denotes parameters of the Chapman-Jouguet zone. In calculating the detonation velocity of pure hydrazine, it has been assumed that all of the hydrazine has been converted to nitrogen and hydrogen.

\[ \text{N}_2\text{H}_4 \rightarrow 2\text{H}_2 + \text{N}_2 \quad \Delta \text{E} = -25.62 \text{ kcal/mole at } 340 \text{ K.} \]

Table I

Computed Detonation Parameters

\( p_1 = 90 \text{ mm Hg.} \)

<table>
<thead>
<tr>
<th>% N₂H₄</th>
<th>T₁ (°K)</th>
<th>T₂ (°K)</th>
<th>( \frac{v_1}{v_2} )</th>
<th>T₆-K (v₁/v₂)C-J</th>
<th>NO %</th>
<th>OH %</th>
<th>O %</th>
<th>D m/sec</th>
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<tr>
<td>0</td>
<td>316</td>
<td>1483</td>
<td>9.24</td>
<td>2555</td>
<td>1.740</td>
<td>2.94</td>
<td>-0.62</td>
<td>1 683 6.11</td>
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<tr>
<td>10</td>
<td>316</td>
<td>1700</td>
<td>10.36</td>
<td>2995</td>
<td>1.755</td>
<td>4.14</td>
<td>3.46</td>
<td>2.83 933 6.86</td>
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<tr>
<td>20</td>
<td>316</td>
<td>1785</td>
<td>11.35</td>
<td>3228</td>
<td>1.764</td>
<td>3.48</td>
<td>5.79</td>
<td>5.75 2089 7.43</td>
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<tr>
<td>33.3</td>
<td>316</td>
<td>1861</td>
<td>12.43</td>
<td>3337</td>
<td>1.769</td>
<td>1.85</td>
<td>5.62</td>
<td>2.68 275 7.97</td>
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<tr>
<td>80</td>
<td>340</td>
<td></td>
<td>13.15</td>
<td>2674</td>
<td>1.754</td>
<td>0.005</td>
<td>0.06</td>
<td>0.002 594 8.51</td>
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<tr>
<td>100</td>
<td>340</td>
<td>1427</td>
<td>18.15</td>
<td>1935</td>
<td>1.736</td>
<td>-</td>
<td>-</td>
<td>-      488 7.99</td>
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</table>

\( T₁ \) = Initial gas temperature

\( T₂ \) = Temperature behind shock front

\( T₆-K \) = Temperature at Chapman-Jouguet zone

\( \frac{v_1}{v_2} \) = Ratio of specific volumes

\( M \) = Mach numbers with respect to initial gas

The theoretical curve for the detonation velocities is included in fig. 4. The highest of the strongly scattering experimental points tend to be fairly close to the calculated
values, confirming again that actual detonation velocities have been measured. The downward trend of the average of all points indicated that uncontrolled effects have eventually decreased the hydrazine concentration of the gas phase.

VI. DISCUSSION

The purpose of these exploratory investigations was to outline experimental possibilities for future work and to check the methods to be applied. It was demonstrated that this approach holds promise of disclosing some interesting properties of the detonations of hydrazine-nitrous oxide mixtures as well as of pure hydrazine vapor. Evidently, there is a limit of detona-

bility which lies fairly close to 100 vol.% N₂O, and which might show a strong dependence upon initial temperature. All attempts to produce detonations through pure nitrous oxide at initial temperatures of 316 K and initial pressures of 90 mm Hg failed. Under these conditions a temperature of only 1480 K was calculated for the front of virtual detonation (table I), a value much too low to induce a rapid enough decom-

position of pure nitrous oxide. Some shock wave experiments reported by STREHLOW and COHEN (ref. 20) have indicated that, at a shock temperature of 1400 K, adiabatic explosion of N₂O is preceded by an induction period of several hundred microseconds. In order to provide a higher temperature behind the detonation front, viz. a reaction zone short enough to facilitate self-supported detonations, one might raise the initial temperature of the test gas appreciably above the values applying in the reported experiments. This might be assumed in analogy to predictions concerning the decomposition flame of NO. These prediction were verified by preheating
the gas to 900 °C (ref. 13). On the other hand even small additions of hydrazine might bring about a substantial change in the critical parameters for detonation. While studying the critical parameters in the inflammation of cyclohexane-nitrous oxide, Russian workers (ref. 14) found an unusually low threshold fuel concentration of 0.3% C6H12. Similar effects seem to control N2H4-N2O detonations.

The detonation velocity of pure hydrazine reveals an interesting feature: two values are conceivable for this case. Either the detonation velocity is determined by the composition of the reaction products, generally observed in the decomposition of hydrazine (ref. 7, 15):

\[ N_2H_4 \rightarrow NH_3 + 1/2 N_2 + 1/2 H_2 \Delta H^\circ = -34.8 \text{ kcal/mole} \ (T=340 \text{ K}) \]

or by the equilibrium composition, which, because of the inertness of the intermediate product NH3, can be attained only after a long reaction period:

\[ N_2H_4 \rightarrow N_2 + 2H_2 \Delta H^\circ = -22.42 \text{ kcal/mole.} \]

The former case would yield a detonation velocity of 2200 m/sec and is definitively excluded by the present results. The detonation velocity given by chemical equilibrium in the Chapman-Jouguet plane, D = 2488 m/sec, is in close agreement with the experimental values. There is no good reason to assume that hydrazine decomposition in the reaction zone of a detonation occurs according to a different mechanism than in shock waves and flames. The actual processes which control the development of hydrazine detonations are visualized in different experiments (cf. section B).
B. Absorption Measurements in Detonations with Hydrazine

I. INTRODUCTION

Studies of detonation velocities of nitrous oxide-hydrazine mixtures seem to show that, in practically all cases, the composition of reaction products in the CHAPMAN-JCUGUET zone, which determines the detonation velocity, corresponds to chemical equilibrium. It is known, however, that in the temperature range under consideration and within the reaction periods available neither the pyrolysis of pure \( N_2 \) (qualitative detection of NO, see section C) nor that of \( \text{N}_2\text{N}_4 \) leads to an equilibrium composition of reaction products (ref. 7, 15). The thermal decomposition of hydrazine is comparatively well understood and a postulated normal chain mechanism is in good agreement with both the observed over-all rate and stoichiometry of the reaction which is \( \text{N}_2\text{H}_4 \rightarrow \text{NH}_3 + 1/2 \text{N}_2 + 1/2 \text{H}_2 \). Additionally, some data about the pyrolysis of the primary reaction product \( \text{NH}_3 \) have been reported in ref. 7. From this it can be derived that the thermal decomposition of \( \text{NH}_3 \), even in the wake of a detonation front, might proceed quite sluggishly.

Because more accurate data about the reaction behavior of hydrazine and ammonia are available at present, interest has been focused upon processes governing the development of detonations with pure hydrazine. The measured detonation velocity demands that the over-all stoichiometry follows the equation \( \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2 \). Kinetic evidence, on the other hand, suggests a fast conversion with ammonia as a major reaction product,
followed by the slow pyrolysis of NH$_3$. Such a slow consecutive reaction, however, would give rise to an unusually long reaction zone of an order of magnitude which has not been observed hitherto even at low pressures (ref. 9 p. 374, ref. 35 - 38).

An alternative reaction path might include the direct conversion of hydrazine to nitrogen and hydrogen without the intermediate formation of ammonia. Since the species N$_2$H$_4$ and H$_2$ possess absorption spectra in the ultraviolet, with roughly known temperature dependence (ref. 7), an available set-up for photoelectric recording could be used to decide to which degree the one or the other reaction path is preferred in the reaction zone of N$_2$H$_4$ detonations at low pressures.

II. METHODS

Monochromator and optical alignment with the detonation tube (section A) were as described in connection with previous shock-tube experiments (ref. 6, 7). A UV light sheet passed through quartz windows, 21 cm upstream from the closed end. Absorption measurements were made mainly at a wavelength of 2500 Å with a monochromator slit width of about 0.34 mm (dispersion dλ/ds ≈ 36 Å/mm). The effective beam width inside the tube amounted to 1.5 mm allowing a time resolution of 0.6 μsec behind the detonation front and 1.4 μsec for measurements behind the reflected wave (velocities of detonation and reflected wave 2.488 mm/μsec and 1.09 mm/μsec, resp.). The actual rise times of the absorption signals behind the fronts of the detonations and reflected shocks were 5 and 10 μsec, resp., indicating again strong curvature or tilt of the
corresponding surfaces (see fig. 5, the same result as with scilemen effects, cf. p 9).

Calibration of the light intensity was made with a rotating sector of 2.8 kc/sec. In this case, however, the intensity recorded with the empty tube was not identical with the characteristic quantity \( I_0 \), on the basis of which the transmission change during an experiment is calculated. As the tube was filled with hydrazine vapor, a film of liquid hydrazine was deposited on the walls and also on the quartz windows. This film reduced the intensity of the incident light appreciably and was not affected by the detonation in the gas phase.

Even when evacuating the tube, it evaporated only reluctantly, as shown by the slow regain of the full light intensity.

Hence, prior to an experiment and after the tube had been filled, the intensity of the transmitted light \( I_1 \) was measured. During experiments at starting pressures of \( P_1 = 90 \) mm Hg, practically all light absorbing species composed behind the reflected wave, so that the oscilloscope trace approached a level which was identified with the one corresponding to full light transmission \( I_0 \) without any absorption from the gaseous phase (cf. fig. 5a). The difference \( I_0 - I_1 \) could be read from the oscilloscope records and the molar absorption coefficient of hydrazine at 340 \(^\circ\)K could be calculated. It was found to be \( \epsilon \cdot x = 1.0 \cdot 10^5 \) cm\(^3\)/mole (\( x = \) geometric path length). Knowing the extinction coefficient of unreacted hydrazine, the value of \( I_1 \) and the gas pressure made it possible to derive the value of \( I_0 \) also for experiments which did not show full light transmission on the oscilloscope (fig. 5b - d).
The trigger to the oscilloscope was provided by one of the schlieren stations, described in section A. The detonation speed was examined on the basis of the time difference recorded between passage of the detonation and of the reflected wave through the UV light beam. Other details of the experimental procedure and of computing the reaction conditions have been mentioned in section A.

III. RESULTS

The oscilloscope records in fig. 5 illustrate the absorption traces behind detonations of hydrazine at four different starting pressures. The sweep speed was 50 \( \mu \)sec/cm, the vertical deflection 0.2 V/cm. The horizontal straight trace corresponds to the initial absorption through hydrazine. Upon arrival of the detonation front, the absorption increases. This, however, cannot be caused by undecomposed hydrazine. Table I (p.11) includes the temperature and density ratio for the shock front of a stable detonation through hydrazine. At a temperature of 1427 \( ^0 \)K and a density of about 8.10\(^{-5} \) mole/cm\(^3\), the expression for the half-lives (ref. 15) \( \tau_{1/2} = \frac{1}{2} \cdot 10^{-14.4} \cdot \exp(+40000/T) \) sec suggests, that most of the hydrazine has been decomposed within less than 1\( \mu \)sec under isothermal conditions and the more so when thermal self-acceleration by adiabatic heat release takes place. Moreover, due to the time compression effect this reaction time appears to the observer to be shortened by a factor which varies between 18 and 3. (In order to transform observed reaction time to a particle time scale, the former has to be multiplied by the density ratio with respect to the initial gas. This density ratio varies across the reaction zone as illustrated by fig. 6).
Fig. 5. Absorption Traces of NH₃ behind Detonations with N₂H₄. \( \lambda = 2500 \text{ Å} \)
Even though the curvature of the detonation front involves a rise time of the initial absorption signal of about 5 μsec, the signal's whole length of about 20 μsec is not accounted for by the absorption of hydrazine. Hence it is ascribed to ammonia.

Following the initial absorption peak, the trace drops off, explainable partly by volume expansion, partly by a decrease in temperature which involves lowering of the extinction coefficient of \( \text{NH}_3 \), and partly by the thermal decomposition of \( \text{NH}_3 \).

After a period of time, which covers 263 to 310 μsec from the passage of the detonation front on, the reflected wave compresses and heats up the reaction products such that renewed absorption is manifested.

The following table summarizes some of the observed quantities from records in Fig. 5. \( P_i \) is the initial pressure of hydrazine at 340 °K, \( \rho_1 \) the gas density in front of the detonation, \( t_r \) is the time elapsed between passage of detonation and reflected wave through the recording light beam, \( I_o \) is the calculated value of the light intensity without any absorption in the gaseous phase. \( I_o/I_i \) is the maximum absorption right behind the detonation front, attributed to an intermediate stage of the reaction, and \( I_o/I_5 \) is the maximum absorption behind the reflected shock wave.

<table>
<thead>
<tr>
<th>( P_i ) [mm Hg]</th>
<th>( t_r ) [μsec]</th>
<th>( I_o[V] \cdot 10^6 \text{ mole} \cdot \text{cm}^{-2} )</th>
<th>( \log I_o/I_i )</th>
<th>( \log I_o/I_5 )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) 90</td>
<td>262</td>
<td>0.49</td>
<td>4.23</td>
<td>0.67</td>
<td>0.36</td>
<td>1.6</td>
</tr>
<tr>
<td>b) 60</td>
<td>290</td>
<td>0.40</td>
<td>2.35</td>
<td>0.44</td>
<td>0.40</td>
<td>1.6</td>
</tr>
<tr>
<td>c) 40</td>
<td>308</td>
<td>0.47</td>
<td>1.23</td>
<td>0.33</td>
<td>0.44</td>
<td>1.7</td>
</tr>
<tr>
<td>d) 30</td>
<td>305</td>
<td>0.56</td>
<td>1.42</td>
<td>0.30</td>
<td>0.48</td>
<td>2.1</td>
</tr>
</tbody>
</table>
The conditions (temperature, density) behind the detonation front are basically unknown, no statements about the NH$_3$ concentrations can be made at this point. Moreover, the curvature of the shock front makes it impossible to measure the initial absorption of decomposing NH$_3$ behind the detonation front (cf. p. 43).

IV. DISCUSSION

Ready detonations are followed by nonsteady rarefaction waves. The distribution of density and local velocity has been dealt with theoretically and experimentally (ref. 39, 40). In this case, however, the starting conditions for the development of these detonations are rather complicated because they are initiated by H$_2$/O$_2$ detonations after rupturing of a diaphragm.

In addition to this, the oscilloscope records of fig. 5 indicate that complete quantities of NH$_3$ are present even at the point where the wake of the detonation interacts with the reflected shock. Since the measured detonation velocity corresponds closely to a theoretical value, which was calculated on the assumption that no NH$_3$ is left in the CHAPMAN-JOUQUET state, one should conclude that the reaction period is not at an end even 260 - 300 $\mu$sec after the detonation front has passed the recording light beam. Under ideal conditions rarefaction waves should not pass beyond the CHAPMAN-JOUQUET region because of the limiting condition for the local flow velocity $K = 1$.

On the other hand, these detonations are not really stable, even though the detonation velocity is reproducible and does not show any dependence upon the composition of the initiator gas.
The series of oscillograms in fig. 5 together with the evaluated data in tab. II illustrate a pronounced pressure dependence of the absorption as well as of the time interval between recording detonation front and reflected wave. This should not be expected for stable hydrazine detonations, because the CHALMERS-JUGUET temperature of 2000 °K is too low to induce any appreciable dissociation of reaction products. Also the density profile in the expansion fan should be independent of pressure in such a case (ref. 39). In these experiments, the reflected waves take more and more time before they cross the UV beam and relatively more and more ammonia appears behind both the detonation front and the reflected shock the lower the starting pressure $P_1$ is.

The variation in the stoichiometry of the reaction is demonstrated by the dimensionless parameters $\alpha$ and $\beta$ (table II).

$\alpha$ represents the logarithm of the measured initial absorption

$$\log \frac{I_0}{I_1} = \varepsilon(T_1) \cdot \varrho_1(NH_3)$$

divided by the initial density of hydrazine $\varrho_1$. $\varepsilon(T_1)$ is the extinction coefficient of NH$_3$ at 2500 $\AA$ and $\varrho_1(NH_3)$ the partial density of ammonia. Measurements of the temperature dependence of NH$_3$ are being made ($\varepsilon(T)$ has been determined only up to wavelengths of 2400 $\AA$ so far, ref. 7). In any case, without assuming a definite stoichiometry of the hydrazine decomposition neither the temperature course nor the profile of total density across the reaction zone can be calculated. But for stable detonations the ratio of densities in the initial gas and at the observable intermediate reaction stage could be expected to be the same at all pressures. This is not born out by the present evaluation as shown by the change in $\alpha$, which indicates an increase in the relative ammonia production with decreasing pressure.
\[ \beta \text{ is defined as the ratio } \frac{\log \frac{I_0}{I_5}}{\log \frac{I_0}{I_1}} = \frac{\xi(T_5) \cdot \rho_5(NH_3)}{\xi(T_1) \cdot \rho_1(NH_3)}. \]

This quantity is a criterion for the amount of NH\(_3\) which has decomposed in the time interval between recording of the detonation front and the reflected shock (subscript 5 denotes parameters behind the reflected shock). Despite the fact that this time interval increases, more and more ammonia survives in the wake of the detonation with decreasing detonation pressure. \(\beta\) grows from 0.53 at \(P_1 = 90\) mm Hg to 1.6 at \(P_1 = 30\) mm Hg. This might be explained in terms of a temperature decrease due to the interaction with expansion waves from both the walls and the initiation end of the tube.

On the assumption that hydrazine decomposes within a fraction of a \(\mu\)sec according to \(H_2H_4 \rightarrow NH_3 + 1/2 N_2 + 1/2 H_2\), followed by the slow pyrolysis of NH\(_3\), and that the effects of expansion waves are negligible within the observation time of about 300 \(\mu\)sec, the course of temperature, density ratio and local mach number have been calculated (fig. 6). As before, indices \(F, i, CJ\) and 5 denote conditions of the initial gas, at the shock front, at the point where hydrazine has decomposed but where all NH\(_3\) is still present (see above), in the CHAPMAN-JOUQUETT state and behind the reflected shock, respectively. It is interesting to note, that the temperature in the reaction zone exceeds the one in the CHAPMAN-JOUQUETT state.

On the basis of this model, one may relate the measured absorption values of NH\(_3\) behind the detonation, to reproduce the profiles of partial density of NH\(_3\) and temperature. Rough estimates indicate a surprising consistency of temperature,
Fig. 6

Detonation Conditions
(with \( D = 2.488 \text{ mm/μsec} \))
governed by the reaction
\[
N_2H_4 \rightarrow NH_3 + 1/2H_2 + 1/2N_2 \rightarrow N_2 + 2H_2
\]

\( P_1 = 90 \text{ mm Hg} \)
\( P_F = 9.0 \text{ atm} \)
\( P_1 = 2.85 \text{ atm} \)
\( P_{CJ} = 1.21 \text{ atm} \)
\( P_5 = 2.86 \text{ atm} \)

\( T_F = 1427 \text{ °K} \)
\( \frac{T_F}{T_{CJ}} = 2619 \text{ °K} \)

\( T_{CJ} = 1995 \text{ °K} \)

\( N_2H_4 \)

\( T_i = 340 \text{ °K} \)

\( \frac{t}{t_F} = 268 \mu\text{sec} \)

\( \frac{P}{P_1} = 1.21 \text{ atm} \)

\( \frac{P_1}{P_{CJ}} = 2.86 \text{ atm} \)

\( \frac{P_{CJ}}{P_5} = 1.74 \text{ atm} \)

\( \frac{P_5}{P_1} = 1.21 \text{ atm} \)

\( \frac{P_1}{P_F} = 9.0 \text{ atm} \)

\( \frac{P_F}{P_{CJ}} = 2.488 \text{ mm/μsec} \)

\( \frac{P_{CJ}}{P_5} = 1.74 \text{ atm} \)

\( \frac{P_5}{P_1} = 1.21 \text{ atm} \)

\( \frac{P_1}{P_F} = 9.0 \text{ atm} \)

\( \frac{P_F}{P_{CJ}} = 2.488 \text{ mm/μsec} \)

\( \frac{P_{CJ}}{P_5} = 1.74 \text{ atm} \)

\( \frac{P_5}{P_1} = 1.21 \text{ atm} \)

\( \frac{P_1}{P_F} = 9.0 \text{ atm} \)

\( \frac{P_F}{P_{CJ}} = 2.488 \text{ mm/μsec} \)

\( \frac{P_{CJ}}{P_5} = 1.74 \text{ atm} \)

\( \frac{P_5}{P_1} = 1.21 \text{ atm} \)

\( \frac{P_1}{P_F} = 9.0 \text{ atm} \)

\( \frac{P_F}{P_{CJ}} = 2.488 \text{ mm/μsec} \)

\( \frac{P_{CJ}}{P_5} = 1.74 \text{ atm} \)

\( \frac{P_5}{P_1} = 1.21 \text{ atm} \)

\( \frac{P_1}{P_F} = 9.0 \text{ atm} \)

\( \frac{P_F}{P_{CJ}} = 2.488 \text{ mm/μsec} \)

\( \frac{P_{CJ}}{P_5} = 1.74 \text{ atm} \)

\( \frac{P_5}{P_1} = 1.21 \text{ atm} \)

\( \frac{P_1}{P_F} = 9.0 \text{ atm} \)
density and kinetic data of the \( \text{NH}_3 \) pyrolysis, known from previous measurements (ref.7). The calculated value for the speed of the reflected shock, travelling through the detonation wake in the CHAPMAN-JOUGUET state is \( u_\text{5} = 1.15 \text{ mm/\mu sec.} \)

(Calculation of the conditions behind the reflected shock in fig. 6 is based on the assumption that the reaction has come to an end before the reflected shock appears, such that any further reaction behind the reflected shock could be ignored. The dissociation \( \text{H}_2 \rightarrow 2\text{H} \) was accounted for. Fig. 6 applies only to an idealized stationary detonation). Further approximate calculations show that the speed of the reflected shock is scarcely influenced by amounts of unreacted ammonia in the wake or by expansion waves from the initiation end (estimated according to ref. 39). \( u_\text{5} \) varies between 1.15 and 1.07 \( \text{mm/\mu sec.} \)

This result in computed values for the time interval \( t_\text{r} \) between 268 and 275 \( \mu \text{sec.} \). The experimental values for \( P_1 = 90 \text{ mm Hg} \) range from 263 to 270 \( \mu \text{sec.} \). This consistency is most likely fortuitous and has to be examined more stringently. At lower initial pressures than \( P_1 = 90 \text{ mm Hg} \), the observed values for \( t_\text{r} \) are as high as 310 \( \mu \text{sec.} \). This suggests that other effects are operative besides phenomena associated with stationary one-dimensional detonations.

Within these cursory studies an interesting type of detonation has been considered. The gradual variation of the quantities \( t_\text{r}, \alpha \) and \( \beta \) with pressure suggests that all of these detonations under the conditions used are inherently unstable despite reasonable values for the instantaneous detonation velocity. Nevertheless, one may expect, that under more favourable initial conditions they become stable.
C. Results from Shock-Wave Studies of the Decomposition of $N_2O$

I. INTRODUCTION

To interpret the observations of hydrazine-nitrous oxide detonations reported in section A, a more intimate knowledge of the thermal decomposition of both hydrazine and nitrous oxide is required. For this purpose, some results of shock-tube experiments with $N_2O$ might ultimately provide supplementary information, apart from the fact that they are interesting for themselves.

The kinetics of the $N_2O$ decomposition has been the subject of a number of investigations. The results of studies at temperatures below 1100 °K have been summarized by JOHNSTON (ref. 17). Some work has been devoted to details of the initial activation process in the unimolecular reaction (ref. 18 - 20) and to the individual rates of secondary steps (ref. 21 - 23). These have indicated a number of uncontrolled complications, which preclude any extrapolation from these data to higher temperatures. Investigations at high temperatures have introduced some interesting technical innovations but have yielded somewhat divergent results (ref. 24 - 26). The shock-tube experiments in process are expected to provide some reliable information. Because the $N_2O$ decomposition is exothermic, reflected shock waves had to be used (ref. 7).

II. EXPERIMENTAL

The same shock tube including the photoelectric recording technique used for the investigation of hydrazine and ammonia and described in ref. 6 and 7 serves for the reexamination of
the \( N_2O \) decomposition. As outlined before, shock parameters were calculated by iteration from the velocity of the incident shock, the attenuation of which was known.

In preparing the test gas, the flow velocities of Ar and \( N_2O \) (controlled by means of capillary flow meters) were set in the desired proportion. The gases were mixed before they entered the evacuated shock tube. Nitrous oxide (cf. p.7) and tank argon for welding (ref. 7, p.41) were used without further purification.

Two series of measurements at two different pressures can be reported now, both covering a range of Mach numbers from 2.55 to 2.80, involving reflected shock temperatures between 1550 and 1850 \( ^\circ \)K at reaction pressures of about 2 and 6.6 atm. Records of \( N_2O \) reactions at temperatures higher than 1850 \( ^\circ \)K have been excluded in the present report because of uncertainties in the reaction conditions. Gas mixtures investigated so far contained 0.9 and 1.9 mole\% \( N_2O \) in Ar. Such high concentrations involve considerable thermal effects during the time in which they react behind reflected shock waves. A simple estimate of these reaction conditions, based upon interpolation between two cases of stationary reactive flow that are amenable to exact computation, has been outlined in ref. 7. This method, however, requires knowledge of the final product composition (\( N_2 \), \( O_2 \) and \( N_3 \)) and of the enthalpy of the reaction. Previous work (ref. 25) did not provide this information. Thus, the present evaluation had to be restricted to the initial stages
of the reaction, where thermal effects are negligible, and
to decompositions that proceeded slowly enough so as not to
accelerate the reflected shock. Thus the initial temperature
of the reaction corresponded closely to the temperature of
the reflected shock calculated by ignoring any reaction
whatsoever. At Mach numbers higher than 2.95, reflected shock
speeds were measured which revealed a definite acceleration
of the reflected wave. Thus, besides records of the reaction
rate, another criterion was available to determine the point
up to which the initial reaction conditions could be given
by the simple shock-wave theory. Possibilities for measuring
the exact proportion of NO among the reaction products will
be outlined below (p. 43).

As with hydrazine and ammonia, the density profile of N₂O
was followed on the basis of its absorption of ultraviolet
light at wave lengths between 2250 and 2400 Å. The station
for photoelectric recording was situated 10 cm upstream from
the reflecting plate. The effective beam width of the UV
light amounted to about 0.7 mr. With an average reflected
shock speed of 0.48 mm/μsec, this resulted in a maximum time
resolution of 1.5 μsec. Accordingly, the electrical time
constant of the recording unit was chosen to be 1 μsec.

III. RESULTS

a) Light Absorption of N₂O

It was extremely conducive to the success of these investi-
gations that nitrous oxide exhibits an unexpectedly high increase
of light absorption with an increase in temperature. Literature

27
data or extinction values in the wave-length interval from 2100 \( \AA \) to 2600 \( \AA \) (continuous absorption, ref. 27) at room temperature did not furnish much hope that photoelectric techniques might be useful in this instance. Fig. 7a, b and 8a, b show oscilloscope record of the absorption traces. The base line results from the photocurrent of the full intensity of the incident light (applied after each experiment). The first step of the absorption trace, clearly discernable only for wave lengths \( \lambda < 2300 \AA \) occurred as the incident shock front passed by. As the reflected wave crossed the recording light beam, strong absorption appeared with subsequent decomposition of \( N_2O \) at a rate which depends upon the shock strength.

Despite the long rise time of the absorption signals (occasionally up to 10 \( \mu \)sec), indicating curvature and tilt of the shock fronts, the decomposition of \( N_2O \) proceeded so slowly at temperatures below 1800 \( ^\circ \)K that reliable evaluation of the initial absorption was possible. Fig. 9 shows the derived extinction coefficients in dependence upon computed temperatures. For the monochromator the following slit widths were used at the various wave lengths involving the dispersion values given below:

\[
\begin{array}{cccccccc}
\lambda [\AA] & 2200 & 2250 & 2300 & 2400 & 2500 & 2600 \\
\delta [\text{mm}] & 0.5 & 0.3 & 0.2 & 0.18 & 0.16 & 0.12 \\
d\lambda/d\delta [\AA/\text{mm}] & 22 & 24 & 27 & 31 & 37 & 42 \\
\end{array}
\]

The increasing dispersion of the monochromator and the widening of the slit (in order to make up for the decrease in both the sensitivity of the photomultiplier and the intensity of the light source) largely compensate each other, such that the spectral band
Records of Absorption behind Shock Waves with $N_2O$

*Fig. 7*

$a)$ $U_i = 0.874 \, \text{mm} = 0.531 \, \frac{\text{mm}}{\mu\text{sec}}$ $1.95\% N_2O$ $\lambda = 2300 \, \text{Å}$

$U_5 = 0.532$ $\phi_5 = 9.6 \cdot 10^{-7} \frac{\text{mole}}{\text{cm}^3}$ $I_0 = 1.9 \, \text{V}$

$T_5 = 1755 \, \text{K}$ $k = 2.6 \cdot 10^3 \, \text{sec}^{-1}$ $\epsilon_{N_2} = 2.1 \cdot 10^5 \frac{\text{cm}^3}{\text{mole}}$

*b) $U_i = 0.876 \, \text{mm} = 0.533 \, \frac{\text{mm}}{\mu\text{sec}}$ $1.92\% N_2O$ $\lambda = 2250 \, \text{Å}$

$U_5 = 0.533$ $\phi_5 = 8.9 \cdot 10^{-7} \frac{\text{mole}}{\text{cm}^3}$ $I_0 = 2.0 \, \text{V}$

$T_5 = 1758 \, \text{K}$ $\epsilon_{N_2} = 3.0 \cdot 10^5 \frac{\text{cm}^3}{\text{mole}}$

sweep $200 \, \mu\text{sec/cm}, 0.5 \, \text{V/cm}$

*Fig. 8*

*a) $U_i = 0.958 \, \text{mm} = 0.532 \, \frac{\text{mm}}{\mu\text{sec}}$ $1.55\% N_2O$ $\lambda = 2400 \, \text{Å}$

$U_5 = 0.532$ $\phi_5 = 5.2 \cdot 10^{-7} \frac{\text{mole}}{\text{cm}^3}$ $I_0 = 1.7 \, \text{V}$

$T_5 = 2080 \, \text{K}$ $k = 1.5 \cdot 10^4 \, \text{sec}^{-1}$

*b) $U_i = 0.955 \, \text{mm} = 0.533 \, \frac{\text{mm}}{\mu\text{sec}}$ $1.54\% N_2O$ $\lambda = 2250 \, \text{Å}$

$U_5 = 0.533$ $\phi_5 = 5.2 \cdot 10^{-7} \frac{\text{mole}}{\text{cm}^3}$ $I_0 = 1.6 \, \text{V}$

$T_5 = 2070 \, \text{K}$

sweep $100 \, \mu\text{sec/cm}, 0.5 \, \text{V/cm}$

Records of Emission during $N_2O$ Pyrolysis

*Fig. 9*

*a) Half-width of the first stage $200 \, \mu\text{sec}$

$b) \, 1.8\% N_2O$

sweep $200 \, \mu\text{sec/cm}, 0.2 \, \text{V/cm}$
width is of the same magnitude throughout the wave-length interval.

In general, data from incident and reflected shocks match satisfactorily. No systematic dependence upon pressure or concentration could be detected.

In fig. 10 the averaged extinction coefficients have been re-plotted versus wave length in order to illustrate the broadening of the whole absorption band with increasing temperature.

b) Light Absorption of NO

At wavelengths around 2250 Å, the absorption trace does not fall back to the zero line, as illustrated particularly by fig. 8 b. Since some bands of the 7-system of NO are situated in this region (0,0 and 1,1 transition) the persisting absorption might be caused by the reaction product NO (the fall-off in fig. 7b is probably caused by cooling and expansion waves, the effect of which is shown because of the slow sweep speed of 200 μsec/cm). Data about the kinetics of the NO decomposition behind shock waves (ref. 28) suggest that the rate determining reaction 2 NO → N₂ + O₂, with \( k = 4.8 \times 10^{23} \cdot T^{-5/2} \cdot \exp \left(-85 \, 500/RT\right) \) cm³/mole·sec would involve a half-life of NO not shorter than 0.1 sec below 2000 °K, as soon as N₂O has disappeared. Hence, the reaction product can be considered as practically stable behind these reflected shock waves, even though the equilibrium proportion of NO at 2000 °K is not more than 1 mole% of the sum of N₂ and O₂. The concentration of NO appearing at the end of the N₂O decomposition can be determined from the remaining absorption at this point if the extinction coefficients of NO are known. This will also provide knowledge of
Fig. 9. Effective absorption coefficient of nitrous oxide vs. temperature

- $\lambda = 2200 \ \text{Å}$
- $\lambda = 2300 \ \text{Å}$
- $\lambda = 2500 \ \text{Å}$
- $\lambda = 2600 \ \text{Å}$
Fig. 10. Effective extinction coefficients of Nitrous Oxide vs. wave length
the stoichiometry and of the enthalpy of the \( \text{N}_2\text{O} \) decomposition. Then the exact reaction conditions are accessible to computations, and investigations can be extended to appreciably higher temperatures. Experiments for the quantitative determination of the light absorption by nitrous oxide at high temperatures are in progress.

c) Initial Decomposition Rates of \( \text{N}_2\text{O} \)

Since the over-all heat of the \( \text{N}_2\text{O} \) reaction is still unknown under these conditions, it would be premature to evaluate the whole of the absorption trace from kinetic aspects. The initial rate of decomposition, however, will not be affected by thermal self-acceleration. The major steps in the thermal decomposition of this quasi-unimolecular reaction are generally believed to be (ref. 21, 24, hot atoms as suggested in ref. 20, will be insignificant with an excess of inert gas):

\[
\begin{align*}
(1) & \quad \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} \\
(2) & \quad \text{O} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2 \\
(2') & \quad \text{O} + \text{N}_2\text{O} \rightarrow 2 \text{NO} \\
(3) & \quad \text{NO} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{NO}_2 \quad k_3 = 2.5 \cdot 10^{14} \exp(-50000/RT) \text{cm}^3/\text{mole} \cdot \text{sec} \\ \\
(4) & \quad \text{NO}_2 + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2 + \text{NO} \\
(5) & \quad \text{M} + \text{O} + \text{NO} \rightarrow \text{NO}_2 + \text{M} \quad k_5 = (2 \text{ to } 4) \cdot 10^{16} \text{cm}^6/\text{mole}^2 \cdot \text{sec} \\ \\
(5') & \quad \text{O} + \text{NO} \rightarrow \text{NC}_2 + \text{O}_2 + \text{hv} \\
(6) & \quad \text{M} + \text{O} + \text{O} \rightarrow \text{O}_2 + \text{M} \quad k_6 = 2 \cdot 10^{17} \cdot T^{-1} \text{ cm}^6/\text{mole}^2 \cdot \text{sec} \\
\end{align*}
\]

No other rate constants than \( k_3, k_5 \) and \( k_6 \) are known with any certainty. Some further thermal decomposition steps of \( \text{NO}_2 \) (ref.32)
are irrelevant for the consideration of the initial reaction rate of $N_2O$. The radiative recombination of $NO$ and $O(5')$ forming $NO_2$ was estimated to account for only a small fraction (about $10^{-3}$) of the termolecular reaction (ref. 21).

For the disappearance of $N_2O$, the following rate expression results:

$$- \frac{d[N_2O]}{dt} = k_1 \left[ N_2O + (k_2 + k_2') [N_2O][O] + k_3 [N_2O][NO] + k_4 [N_2O][O_2] \right]$$

In evaluating initial rates, it is sufficient to assume that $[O]$, $[NO]$ and $[NO_2]$, as well as additional terms which account for thermal self-acceleration, increase linearly with time:

$$- \frac{d \ln [N_2O]}{dt} \propto k_1 + \alpha t$$

The oscilloscope records (such as fig. 7a and 7b) were smoothed and plotted in a concentration scale. By taking the difference $\Delta \ln [N_2O]$ per time $\Delta t$ in the various reaction stages, one was able to extrapolate to the point $t = 0$, the beginning of the reaction, thus obtaining the first-order rate constant $k_1$, which is assigned to the unimolecular decomposition of $N_2O$. Because of the slow rise time of the absorption signals, conditions at the start of the reaction were somewhat obscured in the records. Fig. 11, however, is a typical extrapolation plot for $k_1$, which illustrates that this procedure will not be compromised by too large an error. There is a monotonous increase of the formal first-order rate constant with time up to the point where the evaluation of the oscilloscope records becomes impossible because of too low absorption values.
Fig. 11 Extrapolation Plot for Initial Rate, Corresponding to fig. 7a.

Fig. 12 is the Arrhenius plot of these initial rate constant derived in this way. Data from experiments at temperatures between 1530 and 1820 °K and at total gas densities of 0.45·10⁻⁴ mole/cm³ suggest a temperature dependence of

\[ k_1 = 10^{10.8} \exp(-50 \text{ 000/cal}) \text{ sec}^{-1} \]

This compares favourably with the rate expression at lower temperatures

\[ k_1 = 10^{10.72} \exp(-59400/K) \text{ sec}^{-1} \]

at gas densities of 0.25·10⁻⁵ mole/cm³ (cf. 17).

Some points from experiments at appreciably higher total gas densities are included in Fig. 12. Because only initial rates are considered here, a comparison with the low pressure results is justified, despite the somewhat different partial densities of N₂O.
At the initial stages of the reactions, different total pressures will affect only the collisional activation of the unimolecular reaction step. Comparison of results from low and high pressure experiments disclose that the unimolecular decomposition of N$_2$O

\[ k_1 = 10^{10.81 \exp(-60000/RT) \text{ sec}^{-1}} \]

**Fig. 12. Arrhenius Plot of the Initial First-Order Rate Constants in the Pyrolysis of N$_2$O.**
is strictly regulated in this temperature range by bimolecular activation, viz. it is close to its low-pressure limit. The activation energy of 60 kcal/mole is still comparatively high as compared to the literature values which range down to 50 kcal/mole. This is contradictory to the predictions of unimolecular rate theory, which requires a fall-off of the activation energy as the low-pressure limit is approached (ref. 33). Implications of the dissociation of N₂O via forbidden triplet states, however, account for the exceptional behavior of this compound and have been discussed in the literature (ref. 18, 20).

Extension of these experiments to higher temperatures might further confirm these data. Assessment of the significance of various secondary reactions will be possible, when we know to what degree the heat of the reaction:

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + \frac{1}{2} \text{O}_2 \quad \Delta H^0 = -19.46 \text{ kcal/mole (300 } \text{OK}) \]

is compensated by the endothermic character of the competing decomposition mode

\[ \text{N}_2\text{O} \rightarrow \frac{1}{2} \text{N}_2 + \text{NO} \quad \Delta H^0 = +2.12 \text{ kcal/mole (300 } \text{OK}) \].

The effect of thermal self-acceleration might possibly even outweigh the catalytic acceleration of the reaction by intermediate products under the present experimental conditions.

d) Spectroscopic Observations inission

Other work has indicated a typical chemiluminescence assigned to reaction (5') of nitric oxide with oxygen atoms (ref. 21, 34). The \( \text{N}_2\text{O} \) is reported to appear as a continuous spectrum extending
from about 4500 to 6500 2. Several experiments were made to ob-
serve the magnitude of this chemiluminescence and its dependence
upon time and temperature during the decomposition of N2O behind
reflected shock waves. Even though this phenomenon has been ob-
served before during the decomposition of N2O, it was not certain
at all, whether it would also appear with an excess of Ar, be-
because added gases were shown to reduce the glow intensity
appreciably (ref. 21).

A 2 mm wide section of the window at the lower end of the
shock tube was imaged onto a RCA 931 A photomultiplier, the
light passing on its way through SCHOTT interference filters
(type Al, λmax = 5620 Å, max. transmission 64 %, spectral half-
width 200 Å, and another one with λmax = 4090 Å, max. trans-
nission 51 %). With the 4090 Å filter, scarcely any vertical
deflection of the oscilloscope trace was recorded. With the
5620 Å filter, however, oscillograms of the kind reproduced in
fig. 7c and 8c were obtained. The shock speeds, concentrations
and partial densities of N2O in fig. 7c and 8c correspond close-
ly to the values given in the legends of fig. 7a, b and 8a, b,
resp. The emission signals are composed of two parts: a larger
stage which commences with the arrival of the reflected shock
and the half-period of which (200 and 60 μsec, resp.) coincides
approximately with the half-lives of N2O (220 and 40 μsec, resp.);
moreover, there is a more persisting but lower luminescence
which fades uniformly some 500 μsec after the passage of the re-
lected shock, probably explainable by cooling effects. The rise
time of the former signal is strongly dependent on temperature.
At 1750 °C (fig. 7c), it takes some 100 μsec to attain its full

38
height; at 2080 °K (fig. 8c), the rise time amounts only to 20 μsec (time resolution in these experiments approximately 4 μsec). Wave length dependence and simultaneity of this glow with the reaction are strong evidence for its being caused by radiative recombination of \( \text{NO} + \text{O} \rightarrow \text{NO}_2^* \rightarrow \text{NO}_2 + \text{hv} \). Consequently, the emission intensity should be given by \( I = k'_f(\text{NO})(0) \), and it might be used to trace the change in the product of the concentrations \([\text{NO}]\) and \([\text{O}]\). Under the present conditions, however, ample self-absorption seems to take place because the magnitudes of the emission signals are determined neither by the initial \( \text{N}_2\text{O} \) concentration nor by the reaction rate.

These cursory emission studies are relevant to this investigation of the \( \text{N}_2\text{O} \) decomposition in so far as the observed rise time to the peak intensities indicates that there is a slow build-up of the \( \text{NO} \) and \( \text{O} \) concentrations, followed by a decrease in either one of them or both. Hence there is a reaction period during which oxygen atoms probably exceed by far their equilibrium concentration.

Further work to investigate the pyrolysis of the oxidizer \( \text{N}_2\text{O} \) at high temperatures is in process.

D. The Thermal Decomposition of Hydrazine in Helium

\[ \text{between 1400}^\circ \text{K and 1550}^\circ \text{K} \]

I. PROBLEM

Investigations of the thermal decomposition of hydrazine behind shock waves, using \( \text{Ar} \) as a carrier gas, have indicated that the decomposition process is governed by a non-branching chain mechanism at partial density of hydrazine of \( 20 \cdot 10^{-8} \text{ mole/cm}^3 \) and in the temperature range from \( 1100^\circ \text{K} \) to \( 1400^\circ \text{K} \) (ref. 6 and 7).
Dependence of the half-lives upon temperature, concentration and pressure could satisfactorily be accounted for by a set of four reasonable rate constants for the elementary reactions, the rate-determining steps being the chain initiation:

\[
N_2H_4 \rightarrow 2 NH_2 \quad k_1 \approx 10^{14} \cdot e^{-60000/RT} \text{sec}^{-1}
\]

and a propagation reaction

\[
NH_2 + N_2H_4 \rightarrow NH_3 + N_2H_3 \quad k_2 \approx 10^{13} \cdot e^{-120000/RTc} \text{cm}^3/\text{mole} \cdot \text{sec}
\]

The temperature dependence of \(k_1\) and \(k_2\) given above allows extrapolation to a region between 1400 °K and 1500 °K. When \(\phi = 20 \cdot 10^{-8} \text{mole/cm}^3\), one may calculate on the basis of an approximate relationship between half-life and these rate constants (ref. 7) that the apparent energy of activation obtained from half-life measurements and the activation energy of the unimolecular initiation step should not differ by more than 5% in the temperature region above 1400 °K.

II. PROVISIONS FOR EXTENDING INVESTIGATIONS TO SHORTER REACTION TIMES

Previous measurements of hydrazine decomposition in Ar were confined for reaction times longer than ca. 15 μsec. Close to the shock front absorption signals were strongly distorted by schlieren-effects. The rise time of the signals upon shock passage amounted to as much as 5 μsec. To account for these effects, some correction procedure has already been given (ref. 6). But the corrections were sometimes of the magnitude of the measured quantity itself. Hence, no reliable kinetic information could be expected about hydrazine at temperatures higher than 1400 °K, where the half-life of the decomposition lies around 15 μsec.

The reliability of these measurements can not be improved unless
one is able to reduce the extent of the schlieren-effect and to account properly for the shock-front curvature. This can largely be achieved by using He as a carrier gas. For the same pressure gradient, the schlieren-effect in He is about eight times smaller than in Ar (refractive index of He $n = 1 + 0.36 \times 10^{-4}$, of Ar $n = 1 + 2.81 \times 10^{-4}$; cf. e.g. ref. 41).

In the absence of schlieren-effects, the rise time of the absorption signals upon shock passage depends upon shock speed and shock-front curvature (defined as the distance along the center line from the shock front to the plane formed by the intersection of the shock front and the shock-tube walls).

Since the gases behind reflected shocks are quiescent, a faster rise time of the absorption signal also entails an improvement in time resolution. The rise time was determined to only a small extent by the effective width of the UV beam, which was 0.5 mm in these experiments (for its experimental determination see ref. 61). Hence, the attainable time resolution would have been 1 $\mu$sec with Ar as carrier gas and 0.35 $\mu$sec with He (the average reflected shock speeds were 470 m/sec and 1400 m/sec, resp.; the electrical time constant of the recording unit was chosen as ca. 0.5 $\mu$sec).

The oscilloscope records in Fig. 13 show passage of the incident and of the reflected shock in Ar (fig. 13a, $M = 2.46$, $u_1 = 794$ m/sec, $0.50\% N_2 H_4$, $T_5 = 1500$ °K, $\tau_{1/2} = 4$ $\mu$sec; for denotation and experimental details see ref. 6 and 7) and in He (fig. 13b, $M = 2.46$, $u_1 = 2,453$ m/sec, $0.49\% N_2 H_4$, $T_5 = 1500$ °K, $\tau_{1/2} = 5$ $\mu$sec).

A strong schlieren spike precedes the absorption increase across the incident shock in Ar. In the case of He, the schlieren effect
Fig. 13a

Fig. 13b
is negligible as compared to the size of the absorption signal. In fig. 13a the rise time of absorption across the reflected shock front is 5 μsec, in fig. 13b it amounts only to 3 μsec. This slow rise time might be caused by the tilting of the shock surface relative to the UV beam or by shock-front curvature. Tilting would have manifested itself by random scattering of the experimental rise times. Since the experimental points show comparatively little fluctuation, shock curvature is more likely the proper explanation. The shock-front curvature, as defined above, would amount to 2.4 mm for Ar and 4.2 mm for He. As in LIN and FYFE'S findings for shock-front curvatures of incident shock waves, it does not seem to depend noticeably upon the shock speed (ref. 42 and 43).

Thus, the advantage of using He as a carrier gas is that the range of experiments can be extended to faster reaction rates. Absence of disturbing schlieren effects makes it possible to account for the displacement in time scale by the shock-front curvature when the reaction periods are comparable in length with the rise time of the absorption signal.

For the purpose of this evaluation, a simplified model of the reflected shock surface has been assumed (a more rigorous treatment of the curvature of the incident shock was given in ref. 43). Cooling which results from the formation of an eventually turbulent boundary layer in the wake of the incident shock before it interacted with the reflected wave, as well as bifurcation patterns and weak schlieren effects were ignored (cf. ref. 7). This was justified in the case of He. The bulging back of the reflected shock surface was approximated by an isosceles triangle, its height being equated with the experimental shock curvature of 4.2 mm, viz. 3 μsec.
in time scale (fig. 14). For the sake of simplicity, the concentra-
tion of hydrazine is assumed to decrease linearly with time from the start of the reaction to its half-period (viz. no in-
duction period):

\[
\frac{\varphi}{\varphi_5} \approx \frac{0.5}{t_{1/2}} \cdot t
\]

(\(\varphi\) = instantaneous value of the partial density of \(N_2H_4\),
\(\varphi_5\) = initial value behind reflected shock; reaction time \(t\)
and half-life \(t_{1/2}\) both in \(\mu\)sec).

![Diagram showing the propagation of the reflected shock and the concentration of hydrazine.](image)

Fig. 14

The relative density of hydrazine along the path of the
UV beam is then

\[
\frac{\varphi}{\varphi_5} = 1 - \frac{0.5}{t_{1/2}} \left[ t + 3(1 - \frac{x}{16}) \right]
\]

t is the time counted from the center of the shock front or in
the oscilloscope records from the point of maximum absorption;
x is the distance from the wall (because of symmetry, this is
taken only to the middle of the tube). Then the apparent degree
of reaction is obtained by integration and normalization
with half of the optical path length (16 mm):

\[
\int_0^{16} \frac{\varphi}{\varphi_5} dx = \frac{0.5}{t_{1/2}} (t + 1.5)
\]

It is obvious that the point of maximum absorption, where
\(t = 0\), does not any longer reflect the absorption of hydrazine
prior to the reaction, as it did in the studies made in the temperature range from 1100 °K to 1300 °K.

Then the induction period of the reaction was appreciably longer than the rise time of the absorption across the reflected shock. Now even at \( t = 0 \), the apparent degree of reaction appears to be \( \tilde{\gamma} = 28.8 \% \) for \( \tau_{1/2} = 2.6 \mu\text{sec} \) and \( \tilde{\gamma} = 7.5 \% \) for \( \tau_{1/2} = 10 \mu\text{sec} \). The initial absorption behind the reflected shock cannot any longer serve as the basis for kinetic evaluation of the oscillograms. Instead of this, the exact concentration of hydrazine was derived from the step in the absorption trace, where the incident shock passed by, utilizing the known shock parameters for incident and reflected waves. The theoretical absorption behind the reflected wave prior to reaction could be computed then by extrapolating the curve for the temperature dependence of extinction coefficients to values beyond 1350 °K (fig. 15).

In practically all experiments with He as carrier gas, the difference between theoretical and measured extinction at the absorption maximum was equal to the apparent degree of reaction \( \tilde{\gamma} \), evaluated by means of the above expression at \( t = 0 \). This shows that the simplified model of the shock surface was a good approximation for the reduction of the present data. The quantity used to characterize the decomposition rate of hydrazine was the half-life \( \tau_{1/2} \). The apparent half-life \( \tau'_{1/2} \) was the time interval between the absorption maximum (\( t = 0 \)) and the point where the measured absorption amounted to the apparent degree of reaction \( \tilde{\gamma} = 1/2 \). From the expression given above, one derives then the
Hence, the displacement caused by the shock-front curvature corresponds to approximately half of the time interval necessary for the absorption signal to rise to its maximum value. The absorption at the point where \( \tau = 1/2 \) was obtained by back-calculation from the measured absorption behind the incident shock, using the known shock parameters and the extrapolated curve of the temperature dependence of the extinction coefficients.

Contrary to conditions at temperatures below 1300 \(^\circ\)K, the absorption of ammonia appearing as a decomposition product of hydrazine could not be disregarded in these experiments. Assuming the stoichiometry of the reaction to be \( \text{N}_2\text{H}_4 \rightarrow \text{NH}_3 + 1/2\text{N}_2 + 1/2 \text{H}_2 \) and using the known extinction coefficients of \( \text{NH}_3 \) (ref. 7, 15), it was found that, as half of the hydrazine had decomposed, the extinction of \( \text{NH}_3 \) amounted to approximately 10% of the extinction of hydrazine. This was accounted for in the present evaluation.

Parameters of the incident and reflected shock waves were calculated as outlined in ref. 7, for \( \text{He} \) and \( \text{Ar} \) containing 0.2, 0.3 and 0.5 \% \( \text{N}_2\text{H}_4 \). The acceleration of the reflected shock wave by the heat evolved during the reaction, was accounted for by assuming the case of stationary reactive flow, this having been shown to be adequate if the reaction goes to completion within less than 50 \( \mu\)sec (ref. 7). Moreover, the correction for non-isothermal character \( \Delta T_e \) was added to the computed shock-front temperature. \( \Delta T_e \) was 1.5\(^\circ\C\), 2.3\(^\circ\C\) and 3.7\(^\circ\C\) for carrier gases.
containing 0.2%, 0.3% and 0.5% \( \text{N}_2\text{H}_4 \), respectively (also for the case of stationary reactive flow, \( \Delta T_e \) depends somewhat upon the flow velocity of the gas).

In evaluating the extinction coefficients behind the incident shock, the initial absorption of hydrazine was always considered.

III. RESULTS

A new shock tube having the same dimensions as the one described previously was used. The aluminum walls, however, had not been eloxized. Thus, it was necessary to check whether this in any way promoted the heterogeneous decomposition of hydrazine under the present conditions. The extinction coefficients measured behind the incident shock and reproduced in fig. 15 demonstrate that this was not the case. Nonetheless, in order to obtain this result, the shock tube had to be flushed with the reactant gases under the initial pressure of an experiment for the same length of time as in previous experiments. Under these circumstances, hydrazine seems to be adsorbed by untreated aluminum to approximately the same degree as by eloxized aluminum. The extinction coefficients measured in He up to temperatures of 830 °K confirm those obtained previously with Ar as a carrier gas.

The half-lives of the reactions in He and in Ar are the same (fig. 16). Thus, within the accuracy of these experiments, the decay of hydrazine above 3 atm. seems to be independent of the nature of the inert gas and of the total pressure. Due to the greater difficulties in the reduction of data at faster reaction rates, the scattering of the points is more pronounced than in
Specification of symbols from measurements in Ar in ref. 7.

- extinction coefficients of $N_2H_4$ in He, measured behind incident shock waves, $P_2 \approx 0.9$ atm.

Figure 1: Extinction coefficients of hydrazine in Ar and in He at $\lambda = 2500$ Å
the experiments reported previously. At temperatures above 1400 °K, no systematic relationship between half-lives and the partial density of hydrazine is detectable. The straight line in fig. 16 corresponds to an apparent energy of activation of 40 kcal/mole and was extended to temperatures of 1550 °K from points obtained previously in the interval from 1100 °K to 1400 °K. The half-lives of the decomposition rates which are supposedly governed to a larger extent by the unimolecular reaction exhibit an activation energy which does not seem to be different from that in the temperature range where the chain reaction has an appreciable share in the overall reaction rate.

IV. DISCUSSION
Despite the strong scattering, the points in fig. 16 clearly indicate that the apparent activation energy characterizing the decomposition of hydrazine above 1400 °K is not appreciably different from 40 kcal/mole. This result is surprising in that it has been shown that the chain reaction does not contribute much to the overall decomposition at these partial densities of hydrazine. Hence, this energy of activation will largely be ascribed to the unimolecular fission of the N-N bond. If E=60 kcal/mole is assumed to be the correct value for the critical energy of the N-N bond fission (ref. 44), then a decrement of about 20 kcal/mole would not agree with predictions of current theories dealing with unimolecular reactions. SLATER'S theory (ref. 33) allows for a difference between measured activation energy and critical bond energy at low pressures.
Fig. 16

Arrhenius Plot of Half-Lives of Hydrazine in Argon and in Helium

- $P_5 = 9.6 \cdot 10^{-8}$ mole/cm$^3$, $P_5 = 3.1$ atm.
  0.32\% $N_2H_4$ in Ar
- $P_5 = 6.7 \cdot 10^{-8}$ mole/cm$^3$, $P_5 = 7.5$ atm.
  0.09\% $N_2H_4$ in Ar
- $P_5 = 2.1 \cdot 10^{-8}$ mole/cm$^3$, $P_5 = 7.2$ atm.
  0.30\% $N_2H_4$ in Ar
- $P_5 = 7.1 \cdot 10^{-8}$ mole/cm$^3$, $P_5 = 3.4$ atm.
  0.22\% $N_2H_4$ in He
- $P_5 = 16.8 \cdot 10^{-8}$ mole/cm$^3$, $P_5 = 3.4$ atm.
  0.49\% $N_2H_4$ in He

$E = 40$ kcal/mole

$E = 60$ kcal/mole
of as much as

$$\Delta E = \frac{n}{2} kT \cdot A_n(\theta) < 17 \text{ kcal/mole at } 1450^\circ K,$$

where $n$ denotes the number of effective modes of vibration (in hydrazine $n = 12$) and $A_n(\theta)$ a factor which depends upon total pressure and varies between 0 (at the high pressure limit) and 1 (at the low pressure limit). $\theta$, the parameter proportional to pressure, is

$$\theta = \ldots \frac{\omega}{\nu} \cdot f_n \cdot \left( \frac{E}{RT} \right)^{(n-1)/2}$$

where $\omega$ represents the collision frequency, $\nu$ a mean vibrational frequency and $f_n$ a factor which, when $n = 12$, is about 7 (ref. 33). For the conditions of the present experiments, one calculates with $E = 60$ kcal/mole and $T = 1450^\circ K \theta = 10^5$, whence follows $A_n(\theta) \approx 0.2$ (ref. 33, p. 136) and $\Delta E \approx 3.5$ kcal/mole. Thus, the apparent energy of activation should be fairly close to the high pressure value. In fact, the experimental result that the reaction is independent of pressure and that there are no inert gas effects would contradict the usual expectations for the behaviour of a unimolecular reaction at its low pressure limit.

SLATER'S theory does not explain the discrepancy of 20 kcal/mole.

KASSEL'S model allows for a larger difference between apparent activation energy and critical energy at low pressures

$$\Delta E = n kT A_s(\theta) < 34 \text{ kcal/mole.}$$

But even this interpretation is suitable only if the reaction conditions are such that a definite decline of the first-order rate constant with pressure takes place.
It is curious that the bond dissociation energy given by Szwarc (ref. 44) was obtained as the activation energy of the bond fission reaction at pressures around 10 mm, which is lower by a factor of $4 \cdot 10^{-3}$ than the pressures prevailing in the present experiments. Thus, despite the higher temperature, these present shock tube investigations should have furnished an apparent energy of activation closer to the high-pressure value than Szwarc's data.

The unexpected result that the activation energy does not change appreciably with temperature has to be examined more closely. To obtain more confidence in these shock-tube data, it is necessary to reduce the extent of deviations from ideal shock behaviour. This might be achieved by using a shock tube of a larger diameter.

E. Description of a New Shock Tube

I. INTRODUCTION

Studies of the pyrolysis of cyanazine, ammonia and nitrous oxide (cf. sections C and D) in a square shock tube, 3.2 cm on the inside, had revealed certain limitations in both the range of experimental possibilities and the reliability of the results. Due to the relatively thick boundary layer, appreciable deviations from ideal shock behaviour appeared, such as attenuation of the shock speed, cooling effects to an extent which could not be ignored as well as a definite curvature in the shock surface. Even though the deviations from ideal behavior of the reflected shock, when interacting with an attenuated gas flow behind the
incident wave, and also the cooling effects could be accounted for semiquantitatively, the shock-front curvature involved a loss in time resolution and prevented the spectrophotometric registration of the concentration just behind the shock front at fast reaction rates. The optical path length of 3.2 cm imposed a lower limit upon the concentrations of hydrazine, these being high enough then to produce material changes in the shock conditions due to the heat evolved and the increase in the number of particles during the reaction. It was necessary to apply corrections and the evaluation of the data was not without complications. Besides that, one cannot rule out that certain uncontrolled factors complicate the hydrodynamics of gas flowing through a pipe of square cross-section. In view of this, it seems obligatory to show that previous results were independent of the peculiarities of the technique.

So, a new shock tube was constructed which allows measurements for which these disturbing effects are greatly reduced. In particular, it was necessary to choose a larger cross-section for the tube.

II. CALCULATION OF THE SHOCK-TUBE DIMENSIONS

It appears that a round aluminum shock tube with 10 cm internal diameter provides a considerable improvement and comparatively clean-cut flow conditions. The dimensions of the high and low pressure parts were designed according to empirical rules concerning the path length for stabilization of a shock wave (ref. 45, 46) and according to the desired observation time of the reactions after shock reflection. For the most part, experiments with large excess of $\omega$ are planned and the tube dimensions were calculated for this purpose. The prospective Mach number
Fig. 17. Wave Diagram for $N = 2.18$ (solid lines) and $N = 3.75$ (dashed lines) in Ar.
range is $2.2 < M < 3.7$, corresponding to initial shock speeds through $Ar$ of $0.7 \text{ mm/\mu sec} < u_1 < 1.2 \text{ mm/\mu sec}$. In the lower Mach number range, the observation time near the reflecting plate is limited by the arrival of the expansion waves from the high pressure part. In the higher range of Mach numbers it is the interaction of reflected shock and contact surface (since in general, the acoustic impedances of driver and test gases are not matched), which sets an end to well-defined reaction conditions near the observation window (Fig. 17). Because of cooling effects, it is not meaningful to permit reaction periods much longer than about 1 msec behind reflected shock waves.

Fig. 17 shows the wave diagram for the described shock tube, consisting of a high-pressure section of 2.80 m length and a 4.20 m long low-pressure part. Conditions for initial Mach numbers $M = 2.18$ and $M = 3.75$ with initial speeds $u_1 = 0.7 \text{ mm/\mu sec}$ and $1.2 \text{ mm/\mu sec}$, resp., have been illustrated. A shock attenuation of 2 %/m has been assumed. Then for the above examples the effective Mach numbers (ref. 7) near the observation window are 2.0 and 3.44, resp., on the basis of which the reflected shock speeds were calculated. Because the exact computation of the velocity across the expansion fan (the corresponding flow conditions are not shown in Fig. 17) is laborious, we took the speed of the first expansion signal from the point of reflection at the end of the driver section to the interaction with the contact surface as being uniformly the maximum speed, which is the sum of the sound velocity through expanded hydrogen $c (H_2, 263 \text{ K})$ and the flow velocity $w$. In the last effect, this gives a lower limit for the length of the useful observation period behind the
reflected shock. Beyond the contact surface, the first expansion signal travels at the sound speed of the Ar gas, which is heated by shock compression, superimposed to the flow velocity w.

Various investigations by other workers (ref. 47, 483) have indicated that the contact surface, despite deceleration of the shock front, moves at an almost constant speed which is determined by the initial shock velocity. The first expansion signal finally enters the quiescent gas behind the reflected shock and changes the conditions at the observation windows.

In the case of faster shock waves, it is not the expansion fan but the wave produced by refraction of the reflected shock at the interface which disturbs the observation. The shock tube was dimensioned so that an observation time of at least 1 msec is possible throughout the projected range of Mach numbers.

It was calculated (ref. 49) that the aluminum tube with a wall thickness of 10 mm would withstand 110 atm. under static conditions. Because of shock stress, it is suitable to admit shock waves which produce only half of this value, viz. 55 atm. behind the reflected shock. Steel flanges were screwed onto the aluminum pipe. The flange thicknesses and screw threads were designed to conform with these stress requirements. The main limitations in using shocks of this strength lie in the instability of the building.

Previous experiments had shown that the behavior of untreated aluminum is not any different than that of eloxized aluminum in contact with hydrazine as far as catalytic decomposition or adsorption is concerned (see p.47). Hence, this tube has not been subject to an eloxization process.
III. ACCESSORIES

Two special valves were constructed which permit an adequate rate for pumping and gas intake, resp. and which, at the same time, close tightly to withstand the pressures behind the shock waves. Another requirement was that they would consist of inert materials, such as aluminum and Teflon in order to preclude any catalytic effect upon the heterogeneous decomposition of hydrazine.

Fig. 20 shows the pumping valve. Its internal diameter when opened is not less than 18 mm so that the tube can be evacuated rapidly. When closed, the plunger is flush with the internal walls of the shock tube. The seal is provided by a Teflon G-ring and proved to be sufficiently vacuum tight. Any leak possibilities from the atmosphere have been excluded by using tombac bellows to connect the screw handle with the plunger.

Use of tombac bellows is not permissible for connecting the movable parts of the inlet valve with the outside, since \( \text{N}_2\text{H}_4 \) reacts spontaneously with copper alloys. A Teflon diaphragm fulfills the same purpose and was shown to be hermetically sealed when fixed in the way illustrated in fig. 21. All metal parts which come into contact with hydrazine are made of aluminum.

A solenoid-operated needle was installed in the axis of the tube so that the diaphragm could be ruptured by remote control (fig. 19). The needle which is 4 mm in diameter, consists of a front section made of an unmagentic metal such as brass and a rear section made of iron. An electric magnet of about 8500 coils surrounds the front section. Upon application of a d. c. pulse of about 1 amp. the iron section of the needle is pulled into the magnet and the
brass tip breaks the diaphragm, which is strained by the driver
gas nearly to its bursting pressure. The whole device, including the
iron shield for the magnet has a diameter of only 15 mm (restricting
the cross-section of the high-pressure part by some 2%) and is
streamlined so that no serious disturbance of the gas flow is to
be expected.

A schematic sketch of the whole set-up is given in fig. 18. It has
been shown (ref. 7) to be necessary to flush hydrazine containing
test gases through the low-pressure section under the initial
pressure of a run until adsorption equilibrium between the aluminum
walls and the gas phase is attained. Then both inlet and outlet
stopcocks are closed simultaneously. In order to facilitate a
one-man operation, a special dumping line has been installed, which
can be turned off by a stop-cock situated in the neighborhood of
the inlet stopcock. BODENHEIM-valves allow regulation of the rate
of pumping and gas intake at in-situ hermetic insulation of the
all-glass system from the atmosphere. Fast evacuation for leak
testing and for removal of adsorbed material from the shock tube
walls is still possible through a short wide-bore pumping line
(see fig. 18).

The low pressure section is equipped with four pairs of windows,
through which the shock velocity and its attenuation are measured
by the schlieren method. The windows are 40 cm apart, the last
one being mounted 4 cm from the reflecting plate. At a distance
of 5 cm from the closed end the low-pressure section, there
are quartz windows through which the reaction is recorded spectro-
photometrically. All windows are fixed flush with the inner walls of
the shock tube.
IV. PROSPECTIVE EXPERIMENTS

Since deviations from ideal shock behavior increase with decreasing shock tube diameter and decreasing initial pressure of the test gas, the advantage of the new tube is clearly that it is possible to extend experiments to lower reaction pressures, possibly \( p_2 < 1 \text{ atm} \). This might give indications concerning the shape of the unimolecular fall-off in the decomposition of hydrazine, ammonia and nitrous oxide. The relatively small shock-front curvature allows better time resolution and gives the opportunity to observe the decline of concentration at an earlier stage of the reaction. Moreover, the longer geometric path length of the UV beam makes it possible to investigate lower concentrations of light absorbing reactant species in \( \text{Ar} \), i.e. conditions under which the reacting system is very close to isothermal. At the same time, it is expected that combination with flash spectroscopy, which allows scanning of the whole spectrum within a few microseconds, might yield further information about the intermediates of the reaction.
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