PROPAGATION OF DETONATIONS IN HYDRAZINE VAPOR

H. J. HEINRICH

16. Abstract

In the range of greater hydrazine vapor pressure, detonation speed depends exclusively on the extent of the ammonia decomposition in the second reaction stage. As vapor pressure decreases, the ammonia disintegration speed becomes increasingly slower and the reaction reached in the reaction zone increasingly decreases until finally, in the vapor pressure range between 53 and 16 Torr, the contribution of the second stage to detonation propagation disappears, and only the first stage remains active. Since the disintegration speed of the hydrazine in this pressure range has decreased markedly, as well, no level, but rather only spinning, detonations occur. Temporary separations of the impact front and the reaction zone in the process lead to fluctuations of the detonation speed.

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Introduction

The disintegration of hydrazine vapor in a decomposition flame has been the subject of many investigations [1-3]. These have shown that the reaction does not complete itself during the formation of nitrogen and hydrogen, as would be the case with the thermodynamic balance, but leads, rather, to an intermediate stage \( \text{N}_2\text{H}_4 \rightarrow \text{NH}_3 - 0.5\ \text{N}_2 + 0.5\ \text{H}_2 \). Apparently the disintegration rate of ammonia is still too low at the flame temperature (~1900°K) to lead to noticeable reactions during the relatively short lifespan of the ammonia molecule. Investigations of kinetic hydrazine disintegration in shock waves [4,5] show that the exothermic disintegration in ammonia, nitrogen, and hydrogen takes place at a greater rate even at relatively low temperatures (>2000°K) while endothermic ammonia pyrolysis does not assume comparable rates until temperatures > 2000°K are reached. It was interesting to investigate how such an intermediate stage reaction—in which the clear separation of the individual steps is demonstrated by opposing heat transformation signs—affects the propagation of a gas detonation.

Execution of Experiments

The investigations to spread gas detonations in saturated hydrazine vapor were carried out in glass tubes about 3.65 m long (inner diameter 20 mm). By varying the experiment temperature, the saturation vapor pressure of the hydrazine could be varied greatly. To this end, the longer part of the tube (about 220 cm) was wrapped with heat bandages. The heating of the rest of the

*Numbers in the margin indicate pagination in the foreign text.
tube (145 cm) took place in an air thermostat. This portion consisted of a steel pipe covered with a heat sleeve (inner diameter 10 cm, length 150 sm). This pipe is divided into three sections by fillets, each 4 cm wide. It is equipped with glass windows through which the flame in the glass tube can be observed. The desired temperature was controlled using several thermoelements attached to the glass tube. Thus, it was possible to maintain a uniform temperature in the entire experiment pipe and to set it at about ±0.5°C.

A fuse wire was used for ignition in several experiments, usually with a detonating C₂H₂/O₂ mixture. A second glass tube to collect the ignition mixture was drawn out at one end to an extent that it could be inserted 6 to 8 cm into the experiment pipe with some play. Its drawn-out end was then sealed as thinly as possible and cemented securely in the experiment pipe with all-temperature araldite resin. Blank tests showed that this ensured a vacuum-proof seal of both systems in relation to each other and, also, against the surrounding environment. The glass floor of the combustion pipe was thin enough to weaken the initiating detonation wave only slightly.¹

The experiments were executed as follows: certain amount of liquid hydrazine (97% pure) was introduced into the experiment pipe through a side piece. The amount of liquid was always measured to ensure that a fluid phase would always be present.

¹The usual method to separate both pipe portions using a strength defined by a foil--stretched between flange connections--did not work here. During heating, flange connections often loosened, accompanied by a buckling of the foil, so that it was no longer possible to guarantee a complete seal. Since the gas pressure could not be measured with the experiment pipe during heating and the possibility of seal control was eliminated, the procedure described above was employed because it did not exhibit this deficiency.
in the pipe at test temperature and so that the saturation vapor pressure was constantly set. Then the liquid was cooled below its freezing point. The pipe was evacuated under a pressure < 0.1 Torr and vacuum sealed. The ignition was set off about 10 to 15 minutes after reaching the desired temperature.

A rotary camera with a drum capacity of 100 cm was used to record the flame spread. Flame movement was photographed on a film moving at a sufficiently high speed and perpendicular to the propagation direction of the flame. In this way, it is possible to obtain a path/time diagram for the flame whose shape permits conclusions on the spreading mechanism of the flame. From the tendency of the flame track recorded at a known film speed, it is possible to determine the corresponding flame propagation speed.

Test Results

Detonation tests were carried out in the vapor pressure range between 14 Torr and 760 Torr (23°C to 113.5°C saturation temperature). At first, we tried to induce the detonation with a fuse wire. In most cases, a barely glowing, blue-violet flame occurred at 760 Torr vapor pressure. This flame had a relatively low propagation speed (between 50 to 100 m/sec). The spontaneous transition of such a deflagration into a detonation occurred only seldom and apparently only when a sufficiently high precompression of the fresh gas was reached by the approaching deflagration. In contrast to this, detonations were the rule where a detonating C₂H₂/O₂ mixture was used to initiate the flame. The test set-up used allowed only limited use of parameters for the initiating impulse wave in the corresponding condition dimensions of the hydrazine detonation. For this reason, detonations in the hydrazine frequently developed with elevated or even lower speed and often necessitated running distances of 2 m and more, before they stationary. Only those
detonations were evaluated whose speed did not change in the last 100 cm of an entire running distance of 365 cm.

Table 1

<table>
<thead>
<tr>
<th>°C</th>
<th>$P_{X,H_2}$ (Torr)</th>
<th>$D$ [m/sec]</th>
<th>$\frac{D}{v \cdot d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>113.5</td>
<td>760</td>
<td>2360</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2360</td>
<td>—</td>
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<td></td>
<td>2365</td>
<td>—</td>
</tr>
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<td>133</td>
<td>2270</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2280</td>
<td>0.91</td>
</tr>
<tr>
<td>48</td>
<td>53</td>
<td>2240</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2230</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2225</td>
<td>1.40</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>1050</td>
<td>2.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1850</td>
<td>3.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2080</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2040</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1980</td>
<td>2.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1970</td>
<td>2.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2000</td>
<td>3.01</td>
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<td></td>
<td></td>
<td>1920</td>
<td>2.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1800</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2040</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1930</td>
<td>3.05</td>
</tr>
</tbody>
</table>

The results recorded in Table 1 show that the speed of stationary detonations decreases as hydrazine vapor pressure diminishes. Spin—a periodic oscillation of the detonation front—is observed regularly at pressures below about 400 Torr. The ratio $\frac{D}{v \cdot d}$, formed from passage height $\frac{D}{v}$ ($D =$ detonation speed, $v =$ spin frequency) and pipe diameter $d$, which represents a characteristic dimension for spin and is generally specific for a given gas combination, increases with decreasing gas pressure. According to a theory developed by Manson [6] and Fay [7], spin may be traced back to stationary gas column translation oscillations. Only certain ratios $\frac{D}{v \cdot d}$ are possible which increase in general value by $3 - 1.9 - 1.35 - 1.1 - 0.9$. It can be seen that this is the case here as well. It was not possible to ascertain completely if detonation takes place without spin.
phenomena at vapor pressures in excess of 400 Torr or whether the
spin frequency is simply too high for the limited decomposition
quality of the arrangement. After several photographs it
appeared, however, as if detonation took place with spin
phenomena even at higher vapor pressures—it is to be noted,
however, that these phenomena had a very high frequency.
Frequently, spin was also observed at the final value during
independent acceleration of a sub-initiated detonation. Spin
occurred only over a short stretch; its frequency increased with
speed and finally became imperceptible.

Below about 25 Torr, spin detonation began to become
unsteady. In several cases it degenerated to common
deflagrations. In other cases it converted into a spinning
detonation with periodically varying speed. The rotary drum
photographs reproduced in Figures 1 and 2 shed light on the
matter. They were taken from different tests carried out under
similar conditions (saturation vapor pressure 16 Torr) and
present the detonation course after segments of the detonation
wave varying in length. Figure 1 shows the last 145 cm of a 85
cm-long final course of a detonation segment. The
detonation entering the picture from the upper right at excessive
speed—resulting from super-initiation—slows down rapidly due to
subsequent rarefaction waves. In the meantime, there is a
constant transfer from very high-frequency to low-frequency spin.
As evaluation of speed on corresponding spin frequency shows, the
ratio between passage height and pipe diameter increases at the
pipe's end from 1.50 over 1.9 to 2.9. No further speed decrease
occurs beyond 2010 m/sec, reached at the pipe's end. This can be
seen from Figure 2. This photograph shows the last 145 cm of a
complete stretch of 365 cm, and, as such, borders on Figure 1.
The detonation enters at a spin from the upper right at a speed
of 1950 m/sec (first dark zone) and then increases again to 2080
m/sec. A second dark zone follows with a speed of 1900 m/sec
followed by a renewed increase to 2040 m/sec. The spin frequency
changes synonymously, so that the passage height-diameter ratio
remains nearly constant with values of 2.94 - 3.03 - 2.99 - 2.85. This type of spin detonation with periodically varying speed were observed constantly in this pressure range as long as the /155 detonation stretch was long enough. The "wave length" of such a fluctuation amounted to about 50 to 70 cm and was not regular.

**Figure 1.** Unstable spin detonation \( (p_{N_2H_4} = 16 \text{ Torr}) \)

↓ represents time; ← represents path

**Figure 2.** Pulsing spin detonation \( (p_{N_2H_4}) = 16 \text{ Torr}) \)

↓ represents time; ← represents path
A brightly glowing shock wave is reflected during the impact of the detonation wave onto the pipe floor. Upon closer observation it becomes clear that the reflected shock wave eminates from a point which the advancing visible flame front has not yet reached. As Wagner and Toennies [8] were able to show, this effect occurs when the impact front and the start of the reaction zone separate--whereas the two are normally very closely connected in the detonation wave. This happens when a greater induction time lies in the range of relatively small reaction speeds--somewhere in the vicinity of the detonation boundaries--between the fresh gas seal in the impact front and the start of the chemical reaction. During reflection on the boundary surfaces, pressure and temperature in the impact front increase so much (nearly doubling) that the reaction can start without substantial time lapse. The moment the impact front hits at the pipe's end is marked very precisely on the film, making it possible to measure the distance between the impact front and the reaction zone. Evaluations for all tests in the vapor pressure range around 20 Torr coincided, each yielding a distance between impact front and reaction zone of 6 to 7 mm. As vapor pressure increases, the coupling of the reaction zone and the impact front becomes closer, so that at 50 Torr the distance was even less than 1 mm, the shortest length which can still be solved with the optic set-up.

Commentary

Diffusion of stationary detonation waves in gases has been described quantitatively by a thermodynamic-hydrodynamic theory developed by Chapman and Jouguet [9] and later formulated by Becker [9] and others. Using the laws for conservation of mass, impulse, and energy and the corresponding condition that the stationary detonation wave--related to the explosions--propagates with sound velocity (Chapman-Jouguet condition), the condition dimensions for complete conversion in the detonation wave can be calculated. They serve to determine the detonation speed.
During calculation, it is constantly necessary to assume that reaction speed inside the detonation zone is high enough to regulate thermodynamic balance. A comparison of the calculated and measured detonation speed in a series of systems showed that this assumption is generally well satisfied. A pressure effect on detonation speed is present only as a result of the pressure dependency of the balance in its final condition. This effect is, however, generally very small.

Drastic deviations from this behavior are to be observed during detonation of hydrazine vapor. Tests have determined that the detonation speed is highly dependent upon pressure. The values found lie considerably below those determined theoretically. A detonation speed of 2490 m/sec is calculated for an initial temperature of 113.5°C (760 Torr), while a speed of only 2490 m/sec was found in the experiment.

To interpret this discrepancy one must assume that the thermodynamic balance is not reached in the CJ-plane of the detonation wave (those planes for which the Chapman-Jouguet-condition are valid). The temperature is high enough to push the balance completely toward nitrogen and hydrogen formation according to N₂H₄→N₂+2H₂. The regulating speed of this reaction running over the intermediate stages is, however, not high enough at the prevailing temperature.

From investigations by Murray and Hall [1] we know that decomposition in the hydrazine decomposition flame proceeds only to the ammonia stage: N₂H₄→NH₃+0.5N₂+0.5H₂. Michel and Wagner [4], who investigated the decomposition of hydrazine in shock waves, can show that hydrazine already decomposes sufficiently rapidly at lower temperatures, while subsequent ammonia disintegration is still relatively slow even at temperatures over 2000°C. In the following we shall discuss the meaning of these findings in interpreting data in this study.
First of all, let us reconsider the course of pressure, density, and temperature in the reaction zone. From Chapman and Jouguet's theory, we know the condition dimensions for pressure $p_{CJ}$ and for specific volume $v_{CJ}$ of the CJ-plane in the $p,v$-diagram given by the contact point $CJ$ of the Hugoniot adiabatic curve for complete conversion ($\varepsilon=1$) with the tangent given by the beginning point $A(p_A, v_A)$ (Figure 3). Accordingly, the speed of the detonation wave is directly proportional to the square root of the slope of the tangent. According to the expanded theory by Zeldowitsch, Doering and v. Neumann [11], the detonation wave is understood as a compression impact coupled with a chemical reaction. This compression impact is kept stationary through constant input of energy from the combustion reaction. It only takes a short time for fresh gas to reach the pressure and temperature of the shock wave in the impact front, and chemical reactions connected with it are negligible at first. The reaction really only begins behind the impact front and then progresses rapidly until the balance is reached in the CJ-plane. The phenomena occuring between impact front and CJ-plane are stationary for the observer moving along at detonation speed and are dependent only on location coordinates. The rarefaction wave beginning directly behind the CJ-plane is, on the other hand, no longer characterized by a stationary condition. If one enters the Hugoniot adiabatic curves for the progressing reaction $\varepsilon = f(\lambda)$ into the $p,v$-diagram, then a curve system is obtained which lies between the Hugoniot adiabatic curves of the compression impact ($\varepsilon=0$) and the Hugoniot adiabatic curves for the reaction ($\varepsilon=1$) obtained in the CJ-plane. The coordinates of the intersection of the tangents $A$-$CJ$ extending out over point $CJ$ together with the individual adiabatic curves reproduce condition dimensions $p,v$, which are assigned to the resulting reactions. In general, the reaction profile obtained in this fashion always shows the same picture: pressure and density are highest value in the impact front and become smaller as the reaction proceeds. The temperature increases and reaches its maximum point shortly before the CJ-plane. As Doering [11] and Brinkley and
Richardson [12], among others, were able to show, the speed corresponding to the thermodynamic balance always occurs in stationary detonations. This is true, as well, when, for some reason, a too low detonation speed with an incomplete reaction is obtained in the reaction zone. The reaction in the area of the rarefaction wave causes an increase in temperature and pressure there mainly because of the heat production connected with it. This reaction finally outweighs the influence of the rarefaction wave and leads to the formation of compression waves. After a time, these push together to form a shock wave with supersonic speed. This wave then penetrates the reaction zone of the leading detonation wave and increases its speed so much that the final speed value for completely regulated thermodynamic balance is obtained.

The course of the reaction in the reaction zone of the hydrazine detonation differs from that of normal cases dealt with above since the chemical reaction takes place in two consecutive stages, distinguished by contrasting signs of the heat tone.²

²The division into two consecutive, independent partial stages is permitted since the first proceeds more rapidly than the second.
In the first stage, hydrazine decomposes exothermically according to the equation:

\[\text{N}_2\text{H}_4 \rightarrow \text{NH}_3 + 0.5 \text{ N}_2 + 0.5 \text{ H}_2; \Delta E_{298} = -33.69 \text{ kcal/mol}.\]

The ammonia formed as a result disintegrates endothermically in the second stage according to:

\[\text{NH}_3 \rightarrow 0.5 \text{ N}_2 + 1.5 \text{ H}_2; \Delta E_{298} = +10.45 \text{ kcal/mol}.\]

The energy supply of the first stage is partially compensated by the energy use in the second stage. Figure 4 shows the calculated course of temperature and density in the reaction zone for the detonation speed found in the experiment for \(D = 2360 \text{ m/sec (beginning temperature 386}^\circ\text{K, P}_{\text{Hydrazine}} = 760 \text{ Torr)}\). This speed was independent of the proceeding reaction. The left

Figure 4. Profile of the reaction zone (\(P_{\text{N}_2\text{H}_4} = 760 \text{ Torr}\))
Key: a) Ammonia content of explosions in mols per decomposition of 1 mol hydrazine   b) Impact front   c) 1st stage   d) 2nd stage   e) CJ-plane

\(^3\text{Calculations were carried out using the } C_p^\circ\text{-values for ammonia calculated by Justi [13]. The thermodynamic data for hydrogen, nitrogen, and hydrazine were taken from the tables by Zeise [14]. Oxygen and nitrogen dissociation was ignored.}\)
ordinate indicates density, the right ordinate indicates temperature. The mole number of the ammonia marked on the abscissa represents a measurement for each of the resulting reaction levels in the first and second disintegration stages. As can be seen, hydrazine is compressed to a value 14.7 times its starting density during heating to 1400°K in the impact front. As the hydrazine continues to decompose—which corresponds to an increasing amount of ammonia in the explosions—temperature increases further and density decreases. At the end of the first disintegration stage, the ammonia mol number and temperature have reached their highest value upon the complete decomposition of the hydrazine. At the beginning of the ammonia disintegration in the second reaction stage, temperature decreases again, while density changes only slightly. The condition dimensions of the CJ-plane are reached upon attaining a residue of 0.575 moles ammonia with a density of $1.8 \cdot 10^{-3}$ g cm$^{-3}$ and a temperature of 2271°K.

Detonation speed primarily depends on the temperature and the average molecular weight of explosions in the CJ-plane. The root from the temperature is directly proportional, the root from the average molecular weight inversely proportional. In Figure 5 we see the calculated values for $T$ and $D$ imposed against the corresponding reaction level at the end of the reaction zone for a starting temperature of 386°K. From this chart, we see that the detonation temperature drops as the level of reaction reached in the reaction zone increases. The detonation speed shows a countercurrent tendency. Its greater value lies at complete disintegration of the hydrazine in the elements, because the reduction of average molecular weights of the explosions have a greater weight with increasing decomposition than is the case as the temperature decreases.

It is evident that a detonation wave can be stable even with the coupling of an exothermic and an endothermic reaction if the thermodynamic balance is not reached in the CJ-plane. As the
reaction progresses further in the rarefaction wave beyond the reaction level reached in the CJ-plane, the temperature sinks even further until the reaction finally stops. Under these conditions, compression waves which stiffen the leading detonation wave cannot form in the area of the rarefaction wave.

![Diagram showing relationship between temperature and detonation speed.](image)

**Figure 5.** Temperature and detonation speed independent of reaction level in the CJ-plane (P\textsubscript{N\textsubscript{2}H\textsubscript{4}} = 760 Torr)

Key: Amount of ammonia in the explosions in the CJ-planes in moles

It is necessary now to consider which stationary condition occurs for the given initial conditions. As described above, thermodynamic considerations allow only the possibility of a stationary situation even with incomplete reaction. The extent of the reaction in the CJ-plane is apparently determined, however, by the kinetics of the ammonia disintegration. If one assigns the corresponding reactions to the detonation speeds found, than it is found that the reaction level of the second stage reached in the CJ-plane becomes smaller and smaller with
declining hydrazine saturation pressure (Table 2). 4

<table>
<thead>
<tr>
<th>( p_{X,U} ) (Torr)</th>
<th>( D ) [m/sec] (measured)</th>
<th>( T_{eq} ) [°K] (calculated)</th>
<th>( \alpha_{eq} ) (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>2300</td>
<td>2271</td>
<td>0.575</td>
</tr>
<tr>
<td>133</td>
<td>2275</td>
<td>2330</td>
<td>0.81</td>
</tr>
<tr>
<td>53</td>
<td>2233</td>
<td>2348</td>
<td>0.90</td>
</tr>
</tbody>
</table>

* \( x_{CJ} \) = Number of moles \( NH_3 \) in the CJ-plane, corresponding to the disintegration equation:

\[
N_3H_4 \rightarrow xNH_3 + \frac{2-x}{2} N_3 + \frac{4-3x}{2} H_1.
\]

Since reaction temperatures vary only little, it is reasonable to interpret this behavior using the assumption of a pressure-dependent disintegration speed of ammonia. This is the case according to investigations by Michel and Wagner [15]. The authors, who investigated ammonia disintegration in ammonia/argon mixtures in shock waves at total gas densities of 1.2 to \( 10 \cdot 10^{-5} \text{ Mol/cm}^3 \), found a unimolecular disintegration of ammonia for the temperature range between 2100°K and 2900°K. The unimolecular speed constant related to the total gas density \( \rho \) amounts to

\[
k = 10^{11.64} \cdot \exp \left( \frac{-79.5 \pm 2.5 \text{ kcal/Mol}}{RT} \right) \left[ \text{cm}^3/\text{Mol} \cdot \text{sec} \right]
\]

and is directly proportional to total gas density. The formula has been used experimentally to calculate the reaction time up to the cessation of the reaction level determined by the measured detonation speed. Only the reaction process in the second stage was taken into consideration for the calculation. Since temperature and gas density decrease continually here, (see Figure 4), the integration of the speed equation could not

4Due to varying initial temperatures, the values for \( p = 133 \) Torr and \( p = 53 \) Torr cannot be taken directly from the corresponding curve in Figure 5. The D- and T-curves for each beginning temperature had to be calculated individually.
be carried out in closed form. Rather, the reaction speeds for the individual reaction levels were calculated taking the temperature and density courses in the reaction zone into consideration. From this, the corresponding reaction times were determined using graphic integration. For the saturation pressures 760, 133 and 53 Torr, we thus determined reaction times of 23, 63 and 105 μsec. These values are certainly too high, if one recalls that reaction zone lengths up to about 10 cm would correspond to them. The applied pre-exponential impact factor—which is valid for the ammonia disintegration in argon atmosphere (argon in large excesses)—is probably too low for the conditions at hand (nitrogen and hydrogen in comparable amounts together with ammonia). For this reason, the calculated absolute value of the reaction time commands less interest than its course, which also remains the same, even if the pre-exponential factor is a different one. According to this, reaction time—and with it also reaction zone length—increases as initial hydrazine pressure drops, indeed by about four times during a decrease in the pressure from 760 to 53 Torr.

While the speed of the detonation wave is influenced greatly by the extent of the second reaction stage, the spin phenomena must regarded primarily in connection with the reaction course in the first stage. According to representations by different authors [7, 16, 17, 18], spin occurs preferably in gas mixtures in which a level detonation cannot be propagated, because the heating in the impact front is not sufficient to allow the reaction to take place with the necessary speed. A stabilization is attained far more through the fact that a pressure peak circulates laterally to the propagation direction of the detonation. This pressure peak increases the temperature so greatly at the point where it penetrates into the leading shock wave, that the reaction there can begin with sufficient speed. In areas of lower pressure, on the other hand, the reaction proceeds very slowly, so that for every rotation, a pocket of more or less uncombusted gas at first remains and ignites.
later. The compression wave which forms from this brings the gas column in the pipe into oscillation. The frequency of this self-excited oscillation corresponds with those of the circulating pressure amplitude and is connected to the reaction time in such a way that high spin frequency corresponds to great reaction speed or low spin frequency corresponds to low reaction speed. The test results can be explained satisfactorily with these conceptions. As the experiment shows, spin frequency becomes smaller with decreasing hydrazine vapor concentration—thus with correspondingly decelerated decomposition speed of the hydrazine. In the course of this process the spin frequency apparently only assumes values which are in agreement with the mechanical spin theory of Manson [6] and Fay [7]. The change of the spin frequency with decreasing detonation speed, discernible in Figure 1, rests upon the same effect, except that here the change in hydrazine decomposition speed is connected to the slowing down of the detonation speed during the transition from a strongly excessive to the stationary value. If one compares the stationary speed \(D = 2010 \text{ m/sec}\) obtained in the process with the calculated value of \(D = 2185 \text{ m/sec}\) for complete reaction in the first stage, then it becomes clear that the reaction does not go beyond the first stage, but rather that it stops before completed hydrazine disintegration. Not even the relatively long induction time of the magnitude 10 \(\mu\)sec for the time between transit of the impact front and beginning of the reaction makes a complete reaction very likely within the reaction zone. The pulsation of the detonation wave observed in the same vapor pressure area is easily explained as a result. The reaction proceeds in the rarefaction wave, which runs behind the reaction zone, and in the process leads—as described above—to the formation of shock waves which accelerate the leading detonation wave until the reaction is once again completely located in the range of the reaction zone. Apparently it only takes a small disturbance to damage the weak connection between the leading impact front and the reaction zone to the extent that a portion of the reaction is moved into the area of the rarefaction wave once more. Thus, we
we obtain a more or less periodic fluctuation of the detonation speed around an average value.

Summarizing, the following picture evolves: In the range of greater hydrazine vapor pressure, detonation speed depends exclusively on the extent of the ammonia decomposition in the second reaction stage. As vapor pressure decreases, the ammonia disintegration speed becomes increasingly slower and the reaction reached in the reaction zone increasingly decreases until finally, in the vapor pressure range between 53 and 16 Torr, the contribution of the second stage to detonation propagation disappears, and only the first stage remains active. Since the disintegration speed of the hydrazine in this pressure range has decreased markedly, as well, no level, but rather only spinning, detonations occur. Temporary separations of the impact front and the reaction zone in the process lead to fluctuations of the detonation speed.

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