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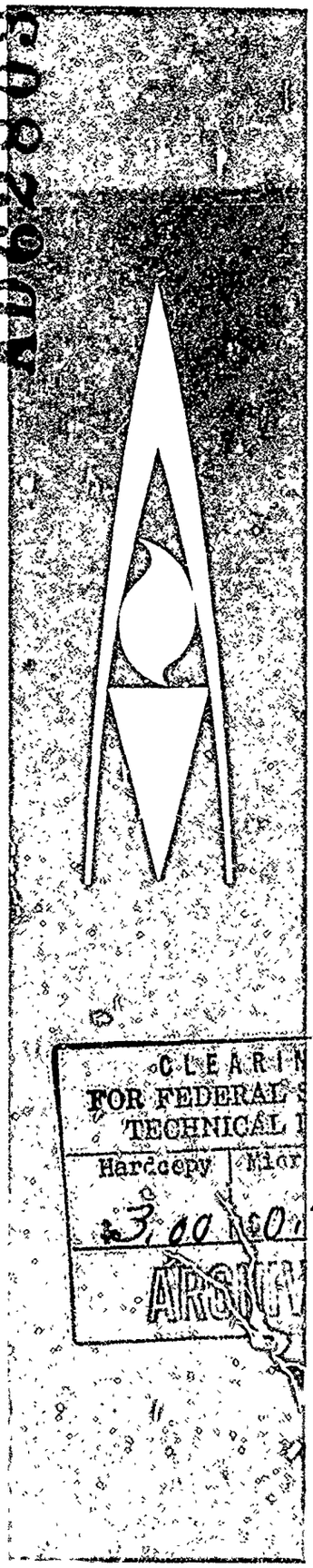

Final Technical Report
June 1, 1962 to November 30, 1965

RESEARCH ON THE DEFLAGRATION OF HIGH-ENERGY SOLID OXIDIZERS (U)

Contract No. AF 49(638)-1169

to
Air Force Office of Scientific Research
Washington, D. C.

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from
Kinetics and Combustion Group
Atlantic Research Corporation
Alexandria, Virginia

November 30, 1965

Chief Investigators: J. B. Levy
G. von Elbe
Internal Consultant: R. Friedman
Chemists: E. T. McHale
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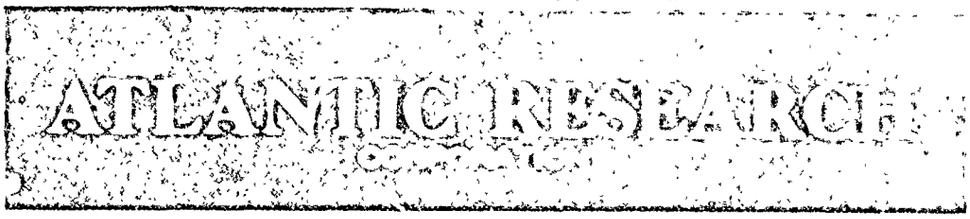

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ATLANTIC RESEARCH CORPORATION
ALEXANDRIA, VIRGINIA

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TABLE OF CONTENTS

		Page
I.	SUMMARY AND ABSTRACT	1
II.	INTRODUCTION	3
III.	HYDRAZINE PERCHLORATE STUDIES	4
	A. Methods of Preparation	4
	B. Determination of Rates of Vaporization	5
	C. Deflagration Rate Measurements	7
	1. The Deflagration of Pure Hydrazine Perchlorate	9
	2. The Deflagration of Hydrazine Perchlorate-Additive Mixtures	9
	D. Measurements of the Temperature Profile	14
	E. Flame Temperature	19
	F. Discussion	23
IV.	HYDRAZINE DIPERCHLORATE STUDIES	26
	A. Experimental	26
	B. Results	27
	1. Deflagration Rate and Effect of Catalysts	27
	2. Flame Temperature	35
	3. Temperature Profile	38
	4. Quenching	42
	5. Thermal Decomposition	43
	6. Chemical Tests	44
	7. Deflagration Experiments in Fuel Gas Streams	46
	C. Discussion	50
V.	REFERENCES	54

ATLANTIC RESEARCH CORPORATION
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I. SUMMARY AND ABSTRACT

The results of research on the deflagration of the solid-propellant oxidizers, hydrazine perchlorate and hydrazine diperchlorate, are reported and discussed. Each compound was found to be unique physically and chemically, in both its low-temperature thermal decomposition and its high-temperature deflagration behavior. Hence, a separation of the results and discussion of each compound is made.

Hydrazine Perchlorate (HP) is a white crystalline solid with crystal density of 1.939 g/cc, which melts at 140-142° C. The experimental work includes measurements of the vaporization rates, deflagration rates, temperature profiles of the deflagration wave, and flame temperature. A limited investigation of the thermal decomposition and chemical behavior of HP was also carried out.

The vaporization rate measurements were performed at temperatures of 180-235° C. The vapor pressure at 200° C, for example, is 2.7×10^{-4} mm Hg (if an evaporation coefficient of unity is assumed) and the enthalpy change for the dissociative vaporization

$$N_2H_5ClO_4(l) \rightarrow N_2H_4(g) + HClO_4(g)$$

was found to be 59 kcal/mole.

Deflagration rates were measured for strands pressed to approximately 95% of crystal density. The deflagration is a non-luminous process and proceeds with a liquid layer but was found to be irreproducible. HP containing 2 to 20% fuel additive was found to deflagrate reproducibly at a rate given by $r = 0.22\ P$ (r in cm/sec, P in atm). The rate was independent of kind or amount of fuel added, and pressure limits of 0.25 to 7.7 atm were observed. Small amounts of certain catalysts augmented the deflagration greatly.

Temperature profiles were obtained by imbedding fine thermocouples in HP strands (containing fuel additive). These experiments showed no evidence of heat release in the condensed phase up to 450° C. The flame temperature of HP containing 2% thiourea and 2% Na Cl was measured by the

sodium-line reversal method. Within experimental error the theoretical and experimental temperatures agreed, and it was concluded that thermodynamic equilibrium was attained in the product gases. The theoretical adiabatic flame temperature at 1 atm for HP is 2246°K and the stoichiometry corresponds closely to

$$N_2H_5ClO_4 \rightarrow N_2 + HCl + 2H_2O + O_2$$

Hydrazine Diperchlorate (HDP) is a white crystalline solid of crystal density 2.21 g/cc, which melts at 190-192° C. The following aspects of the combustion process were studied: The deflagration rate as a function of pressure and the effects of catalysts; the flame temperature and the temperature profile through the combustion wave; quenching, thermal decomposition, and chemical behavior.

As with hydrazine perchlorate, the deflagration is a non-luminous process and proceeds with a liquid layer. The linear rate was found to be: $r = 1.75 \times 10^{-3} P^{1.44}$ from approximately 6 to 100 atm; $r = 0.28 P^{0.28}$ from 100 atm to 350 atm, which was the highest pressure studied. Catalysts were observed to accelerate the rate by more than an order of magnitude in some cases.

The flame temperature (measured by thermocouples) was found to increase with increasing pressure. At 28 atm, $T_f = 1385°K$; at 103 atm, $T_f = 1595°K$. The theoretical temperature at 100 atm was calculated to be 1604°K, and the stoichiometry is approximately

$$N_2H_6(ClO_4)_2 \rightarrow N_2 + 2HCl + 2H_2O + 3\,O_2$$

Temperature-profile measurements of deflagrating strands at various pressures showed that below about 20 atm the profile no longer displayed the shape of that of a normal combustion wave. At pressures lower than 20 atm the results indicate that the oxidizer is consumed by a self-sustaining, rapid decomposition, and that heat transfer from a flame zone is making at most a secondary contribution to the process. The profile through the condensed-phase preheat zone indicated that the thermal diffusivity of HDP decreases with increasing temperature.

Experiments to determine quenching distances are also described, as are thermal decomposition studies and special chemical tests on both HP and HDP. A finding of significance in these tests was that HP and HDP are impervious to attack by chlorine dioxide up to 100° C. Unifying discussions of the HP and HDP results are presented.

II. INTRODUCTION

We are engaged in a general program of research whose goal is the understanding of the factors that govern the nature of the deflagration of composite solid propellants. Our efforts have been devoted to studies of the oxidizer alone, ever since early observations that ammonium perchlorate deflagrated as a monopropellant at rates comparable to those found for propellant formulations containing it (1,2). This suggested that self-deflagration of the oxidizer played an important role in the deflagration of the propellant. Research in this and other laboratories has confirmed this hypothesis. Our earlier work was concerned with ammonium perchlorate and we have reported on its self-deflagration and other aspects of its chemistry that are pertinent to the deflagration process (3).

Under the present contract we have extended studies of oxidizers to compounds that are of present and potential interest as energetic ingredients in solid propellants -- namely, hydrazine perchlorate and hydrazine diperchlorate. Approximately one half of the effort in the program was given to each compound. Each was found to exhibit different chemical behavior and to deflagrate in a manner different from the other and from ammonium perchlorate. The experimental approach to obtaining data necessary for an understanding of the deflagration mechanism varied greatly for the two oxidizers. Accordingly, a natural division of the main body of the final report is made into a section on each, containing separate experimental, results and discussion parts.

Under the contract, a paper entitled "The Deflagration of Hydrazine Perchlorate" was presented at the 149th National Meeting of the American

Chemical Society, Division of Fuel Chemistry in Detroit, April 4-9, 1965. This paper is scheduled for publication in Advances in Chemistry Series in 1966. Another paper, "Gasification by Sublimation, Nucleate Boiling, and Chemical Attack in Oxidizer Deflagration Waves," was presented at the 2nd ICRPG Combustion Conference, November 1-5, 1965. A publication entitled "The Deflagration of Hydrazine Diperchlorate" has been prepared for submission to the Journal of Physical Chemistry.

III. HYDRAZINE PERCHLORATE STUDIES

A. Methods of Preparation

Hydrazine perchlorate (HP) was prepared by titrating a solution of 85% hydrazine hydrate to a pH of 3.2 with 48% perchloric acid. This yielded a stock solution which could be stored indefinitely. The salt was precipitated by pouring a volume of this solution into five volumes of isopropanol at 0° C. The precipitate was filtered, washed with cold isopropanol and vacuum dried at 80° C.

The product was analyzed iodometrically (4). Purities > 99%, as indicated by the analysis, were obtained. The melting point was 142-143° C.

The preparation of strands for deflagration studies was facilitated by forming the material into small pellets. For this purpose, solid HP was fed into a spinning aluminum dish maintained at a temperature above the melting point of hydrazine perchlorate and fitted with a small lateral hole in the side which permitted the ejection of the molten spheres which cool as they fly through the air. It was found that 160° C was a satisfactory temperature for the dish. With the dish spinning at 2400 RPM the particle sizes of the spheres obtained, as determined by microscopic examination of a random selection, varied from 50 - 300μ. Analysis of material prepared in this way indicated that no decomposition occurred during the shotting process.

Strands were either tamped or pressed. Tamped strands were prepared by pouring small increments of material into a tube and tamping each

increment gently with a Teflon rod. Pressed strands were prepared in a steel mold by means of a hydraulic press. Pressures of ~ 40,000 psi gave strands of 95-98% of crystal density. Pressing operations were performed remotely.

Mixtures of hydrazine perchlorate and fuels or catalysts were prepared by mixing the hydrazine perchlorate shot with the finely-ground other ingredients in an ordinary vee mixer for several hours. The uniform deflagration rates observed with the various mixtures attest to the homogeneity of strands prepared in this way.

B. Determination of Rates of Vaporization

Vaporization rates were measured using a cold-finger glass apparatus, with a removable cold finger. The apparatus was evacuated by an oil pump to about 5 microns, lowered into a thermostat and the timer started.

Two sizes of apparatuses were used. At first a fairly small one with a cross sectional area of 0.5 cm^2 was used to keep the amount of hydrazine perchlorate required down to about 0.5 g. Subsequently a larger apparatus having a cross-sectional area of 4.90 cm^2 was used with amounts of hydrazine perchlorate of the order of 1.5 - 2.0 g.

At the conclusion of the experiment the solid condensate was carefully removed from the cold finger and weighed. The weight of the residue was found by weighing the outer tube, washing out the residue and re-weighing the tube. The analyses were performed by iodometry.

The surface area of the molten HP was quite undisturbed by bubbles during these experiments and its magnitude was constant during an experiment. The temperature of the liquid was assumed to be that of the bath in which the apparatus was immersed. The results are given in Table I.

TABLE I

VAPORIZATION RATES OF HYDRAZINE PERCHLORATE

Temp. (°K)	Area (cm^2)	Duration (sec)	Weights in Grams charged	sublimed	residue	% recov.	% Hydrazine Perchlorate in Sublimate	Residue	10^6 × Rate of Vaporization (g/cm^2-sec)
453	4.90	18,900	1.56	0.22	1.32	99	99.8	99.4	2.38
463	0.50	21,240	0.244	0.073	0.163	97			6.85
473	4.90	18,900	1.70	0.54	1.14	99	95.0	99.0	5.84
492	0.50	2,220	0.239	0.036	0.200	99			32.4
508	4.90	2,400	1.65	0.83	0.79	98	99.0	100.0	70.5

The relation between vaporization rate and vapor pressure is given by $g = \alpha P \sqrt{\frac{M}{2\pi RT}}$ (5).

g = vaporization rate in g cm^{-2} sec^{-1}
α = evaporization coefficient
P = vapor pressure in dynes cm^{-2}
M = molecular weight of vaporizing species
T = absolute temperature
R = gas constant in ergs $mole^{-1}$ deg^{-1}

This expression can be written,

$$g\sqrt{T} = \alpha\sqrt{\frac{M}{2\pi R}}\ P$$

For many liquids α has been found to be unity. However a very low value for this quantity has been calculated (6) for ammonium chloride and, since very few species that are chemically similar to hydrazine perchlorate have been investigated, we do not feel justified in assigning a value of unity for α in the present case.

It is of interest to see how the parameter $g\sqrt{T}$ varies with T. Since it is proportional to P, we would expect a Clausius-Clapeyron

relationship to hold, if α were constant, and in Fig. 1 we plot $\log\left(g \sqrt{T}\right)$ vs 1/T. The data are fairly linear and the line in Fig. 1, which was drawn visually, corresponds to the equation:

$$\log_{10}\left(g \sqrt{T}\right) = 10.0 - \frac{6475}{T}$$

The slope of the line is a measure of the heat of vaporization ΔH_v and leads to a value of 29.6 kcal/mole for this quantity. The corresponding value for ammonium perchlorate is 29 kcal/mole (7). It is of interest to compare the above value for ΔH_v to that calculated for the vaporization process. If we consider that hydrazine perchlorate vaporizes with dissociation, as is believed to be true for ammonium perchlorate, the equilibrium is

$$N_2H_5ClO_4\,(l) \rightleftarrows N_2H_4\,(g) + HClO_4\,(g)$$

The enthalpy change for this process would be $2\Delta H_v$ or 59.2 kcal/mole. The heat of formation of crystalline hydrazine perchlorate is -42.5 kcal/mole (8) and a value of 3.84 kcal/mole has been reported for the heat of fusion (9). The heat of formation for the liquid is thus -38.7 kcal/mole. The values for gaseous perchloric acid and gaseous hydrazine are -1.1 (10) and 22.75 kcal/mole (11) respectively. These values yield 60.4 kcal/mole as the enthalpy change in the above equilibrium. The agreement with the experimental value supports our belief that the vaporization rates are proportional to the vapor pressure and that the vaporization process is dissociative.

C. Deflagration Rate Measurements

Strands of HP were topped off with a small quantity of Arcite propellant which was ignited by a hot wire. The Arcite served to initiate the deflagration of the strand. Deflagration rates were measured from motion picture records. The lengths of strands used were in the range of 1.5 - 2.0 cm. In all cases the linear deflagration rate was determined from the slope of the curve of length deflagrated vs. time. These

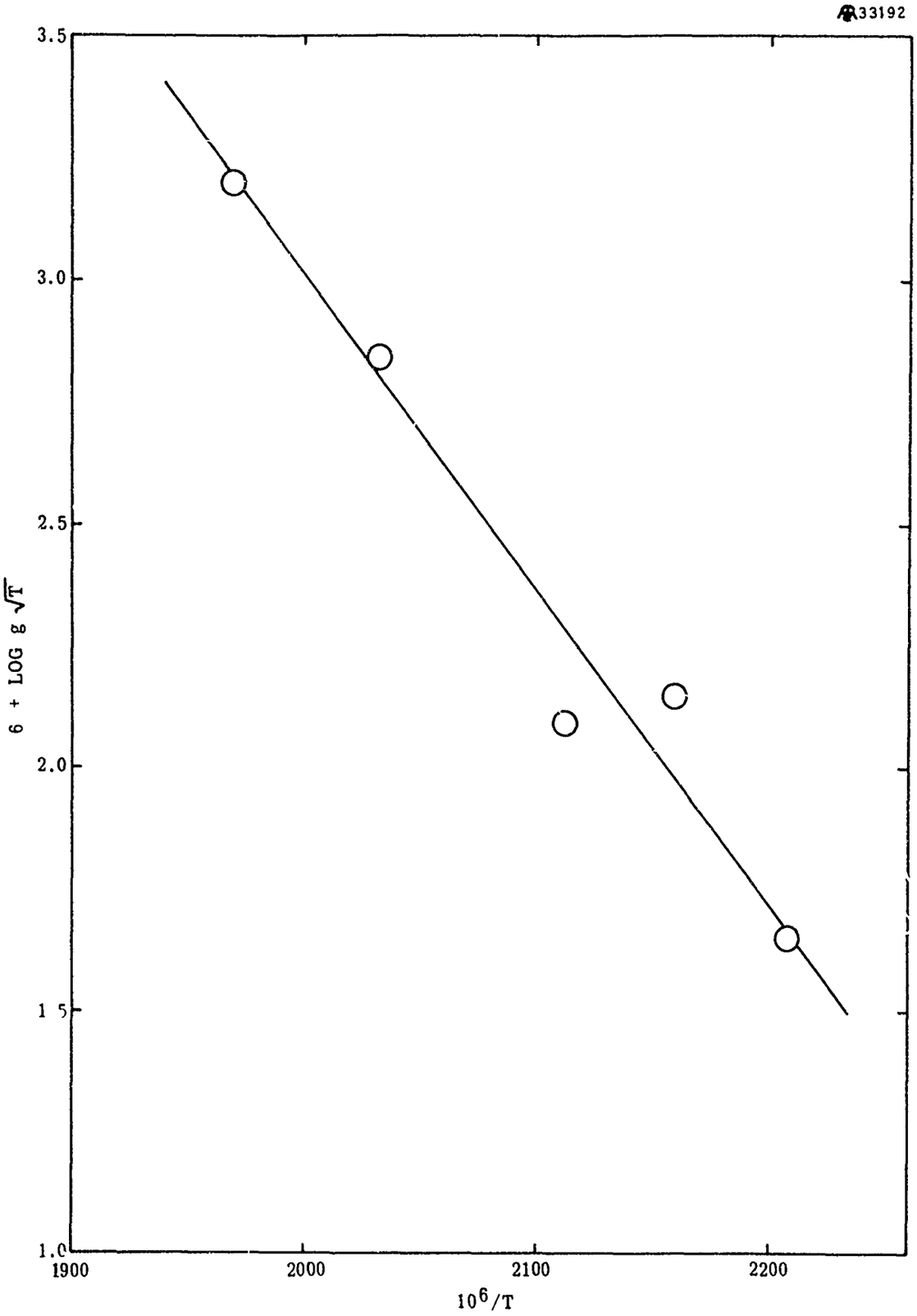

Figure 1. The Rate of Vaporization of Hydrazine Perchlorate.

curves were all linear, i.e., the deflagration rates were constant over the length of the strand. In all the deflagration experiments a molten layer could be seen at the surface of the deflagrating strand. Gas evolution within the layer was so vigorous that the liquid layer never appeared transparent but rather like a foam. The liquid-solid interface was distinct however and the rate measurements were made by measuring the regression rate of this interface.

1. The Deflagration of Pure Hydrazine Perchlorate

The behavior of pure hydrazine perchlorate, i.e., material containing no additives, was not reproducible. Smooth deflagration of tamped (ρ = 1.8 - 1.9 g/cc) strands of hydrazine perchlorate was attained for pressures from 0.25 to 4.3 atmospheres but at a subsequent time a batch of strands prepared and ignited in the same way did not propagate deflagration. When this was observed, experiments were performed with strands preheated to 50° C. Here again, smooth deflagration was attained at two, four and six atmospheres for some batch of strands, whereas another batch failed to deflagrate. A non-deflagrating strand would detonate when exposed at one end to a hot wire for some length of time.

2. The Deflagration of Hydrazine Perchlorate-Additive Mixtures

a. Fuel Additives

In the case of ammonium perchlorate, it has been found (12) that at pressures below that at which pure ammonium perchlorate will sustain deflagration, ammonium perchlorate-fuel mixtures containing of the order of 5% fuel do deflagrate smoothly. Paraformaldehyde was the most effective of the fuel additives in promoting deflagration and for that reason experiments were performed with mixtures of hydrazine perchlorate and various formaldehyde polymers.

Experiments with paraformaldehyde were unsuccessful because it was found that when these additives were mixed with hydrazine perchlorate the mixture became yellow and the consistency changed from that of the original powders to that of a dough. S-trioxane, a more stable formaldehyde polymer than paraformaldehyde, gave a less reactive mixture than

paraformaldehyde, but the results were still unsatisfactory. Del-rin*, a stabilized formaldehyde polymer, proved even less reactive than S-trioxane. Magnesium oxide was added to hydrazine perchlorate-Del-rin mixtures on the theory that acidity in the hydrazine perchlorate might be responsible for the reaction occurring. It was found that mixtures of 94.5% hydrazine perchlorate - 0.5% MgO - 5% Del-rin were stable and a series of experiments was performed with this mixture.

Other fuel-type additives were effective in promoting the deflagration of hydrazine perchlorate. Experiments have been performed with thiourea and naphthalene. The results of the deflagration experiments for preheated pure hydrazine perchlorate and for the hydrazine perchlorate-fuel mixtures are summarized in Table II and Fig. 2. The strands used were all pressed to about 95% of the crystal density, i.e., to a density of about 1.85 g/cc.

Table II

DEFLAGRATION RATES FOR HYDRAZINE PERCHLORATE

No.	Composition	ρ (g/cc)	P (atm)	$\dot{r}$ (cm/sec)	$\dot{m}$ (g/cm^2-sec)
1	5% Del-Rin 0.5% MgO	1.87	0.26	0.01-0.02	0.02-0.04
2	5% Del-Rin 0.5% MgO	1.85	0.52	0.11	0.21
3	pure HP preheated to 69° C	1.87	1.0	0.24	0.45
4	5% Del-Rin 0.5% MgO	1.85	1.0	0.22	0.41
5	5% Del-Rin 0.5% MgO	1.85	1.0	0.22	0.41
6	2% Thiourea	1.86	1.0	0.17	0.32
7	5% Naphthalene	1.83	1.0	0.21	0.38
8	20% Thiourea	1.79	1.0	0.18	0.32
9	preheated to 50° C	1.91	2.0	0.52	0.98
10	5% Del-Rin 0.5% MgO	1.85	3.0	0.56	1.0
11	5% Del-Rin 0.5% MgO	1.85	4.3	0.90	1.67
12	preheated to 50° C	1.91	6.0	1.29	2.48
13	5% Del-Rin 0.5% MgO	1.85	7.0	1.39	2.5
14	5% Thiourea	1.82	7.7	1.73	3.18
15	10% Thiourea	1.81	7.7	1.21	3.1

* du Pont trade name

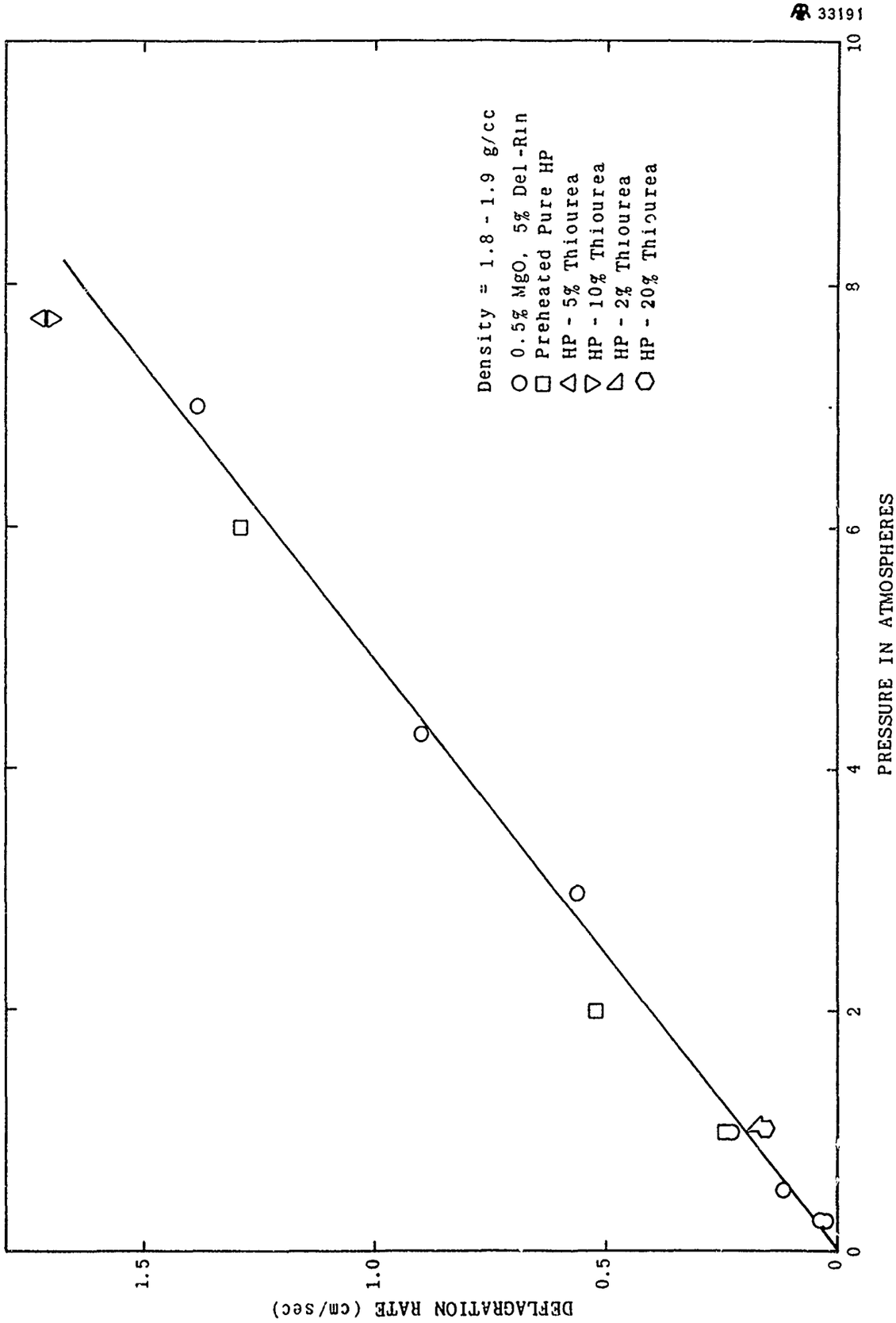

Figure 2. The Rate of Deflagration of Hydrazine Perchlorate With Small Amount of Fuel.

Deflagration rates are given for pressures ranging from 0.26 atmospheres to 7.7 atmospheres. The experiment at 0.26 atmospheres yielded a curve of length-deflagrated vs. time that was somewhat concave upward. The rate cited is thus a rather crude value but is of interest because of the low pressure. All the other rates were constant. Attempts to measure rates at higher pressures than 7.7 atmospheres resulted either in a complete lack of ignition or in a deflagration that proceeded down the sides of the strands leaving a central unburned core.

Figure 2 shows that all the data fall fairly well around a single line, $\dot{r} = 0.22\ P$, where $\dot{r}$ is in cm/sec and P is in atmospheres.

b. The Effects of Catalysts

It has been found that copper chromite, potassium dichromate, and magnesium oxide promote the deflagration of hydrazine perchlorate. Since none of these additives has any fuel content, they must be considered to be catalysts. The results of experiments with these additive species are shown in Table III. Experiments were performed both with pressed ($\rho \approx 1.9$ g/cc) and tamped ($\rho \approx 1.1$ g/cc) strands.

It may be noted that for copper chromite and potassium dichromate a minimum of around 5% catalyst was necessary in order to attain steady deflagration; however when deflagration did occur the rate was high compared to the case for fuel-promoted deflagration. It may be noted too, table entries 2 and 3, that for strands containing 5% copper chromite but having different densities, the mass deflagration rates agree well while the linear rates do not. It thus seems satisfactory to compare mass rates for strands of different densities. A comparison of this type shows that potassium dichromate is a powerful catalyst but not as powerful as copper chromite.

Magnesium oxide exerts quite a different effect than do the above catalysts. Thus less of it, 2%, is required to promote steady deflagration, but it is not capable of producing as spectacular a rate as copper chromite or potassium dichromate, even in amounts as great as 10%.

TABLE III

THE EFFECT OF CATALYSTS ON THE DEFLAGRATION OF HYDRAZINE PERCHLORATE

No.	Composition (% of additives)	ρ (g/cc)	P (atm)	ṙ (cm/sec)	ṁ (g/cm²/sec)
1	2.5% $CuCrO_2$	1.13	1	did not deflagrate	
2	5% $CuCrO_2$	1.10	1	1.20	1.32
3	5% $CuCrO_2$	1.93	1	0.71	1.37
4	5% $CuCrO_2$	1.95	0.52	0.36	0.69
4a	5% $CuCrO_2$	1.93	2	exploded	
5	2.5% $K_2Cr_2O_7$	1.17	1	did not deflagrate	
6	5% $K_2Cr_2O_7$	1.19	1	0.75	0.89
7	2% MgO	1.90	1	0.26	0.50
8	5% MgO	1.91	1	0.21	0.59
9	10% MgO	1.89	1	0.35	0.66
10	20% MgO	1.86	1	partial deflagration	
11	2% CaO	1.31	1	0.12	0.16

The effect of calcium oxide was briefly examined since it is chemically similar to magnesium oxide. A tamped strand deflagrated at 1 atmosphere to give a somewhat lower rate, i.e., as compared to the curve of Fig. 2. Calcium oxide is quite deliquescent and there were indications in this experiment of some moisture absorption.

In a side experiment to see if there was any generality to the effect of magnesium oxide, a tamped strand of hydrazine nitrate containing 2% MgO was found to deflagrate steadily at 0.04 cm/sec (ρ = 0.93 g/cc, $\dot{m}$ = 0.037 g/cc sec) while pure hydrazine nitrate would not propagate deflagration.

D. Measurements of the Temperature Profile

Temperature profiles of the deflagration wave have been made using thermocouples of 0.0005-inch Pt - Pt, 10% Rh wires joined in a fused bead. The voltage changes were recorded by a Visicorder which registers voltage changes by the deflection of a light point on a moving film. The deflagration rates were measured simultaneously so that it was possible to convert temperature-time records to temperature-distance records. The turbulence of the liquid layer as observed in the deflagration rate measurements indicated that one could not expect a smooth temperature-time record. Figures 3 and 4 illustrate the type of record obtained. There are some irregularities in the curves, but the data are not too erratic for analysis.

Fig. 3 shows tracings of the records obtained at 0.5 atmospheres with a pressed strand of 94.5% hydrazine perchlorate, 5% Del-Rin, 0.5% MgO, ρ = 1.85 g/cc and Fig. 4 shows the tracing of the record obtained for a tamped strand of the same composition, ρ = 1.24 g/cc, at one atmosphere. In Fig. 5 and 6 are shown the experimental data converted to a temperature-distance function by means of the measured deflagration rates.

The solid curves in Figs. 5 and 6 are the theoretical curves obtained for indicated values of thermal diffusivity of the solid. The following treatment has been applied. The temperature gradient within the zone bounded by the deflagrating surface on the one hand and ambient temperature on the other can be written

$$k \frac{d^2T}{dx^2} - c\rho r \frac{dT}{dx} + q_c = 0$$

where

k = coefficient of heat conduction
c = specific heat
ρ = density
q_c = heat produced within the zone
T = temperature at point x
r = deflagration rate

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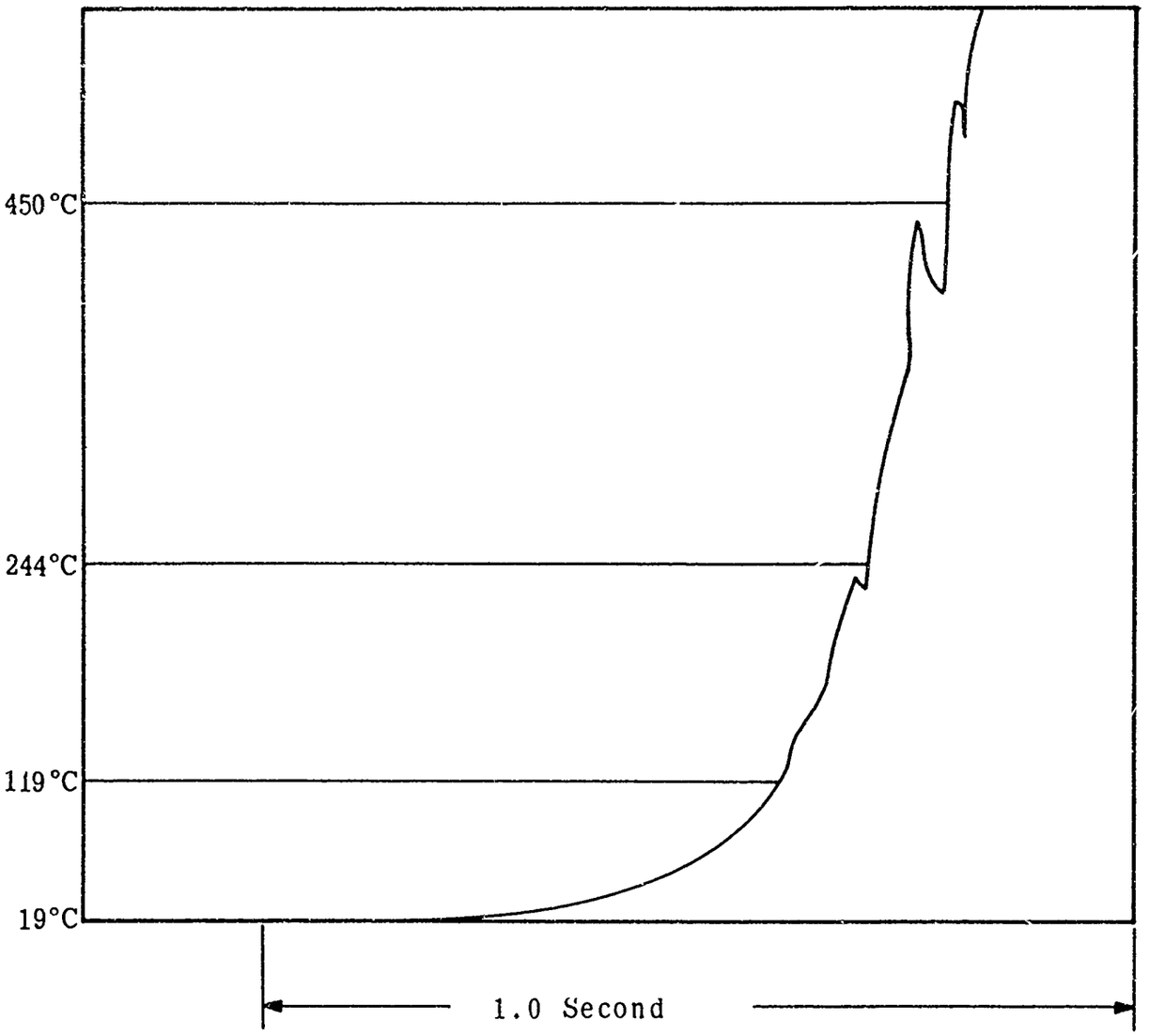
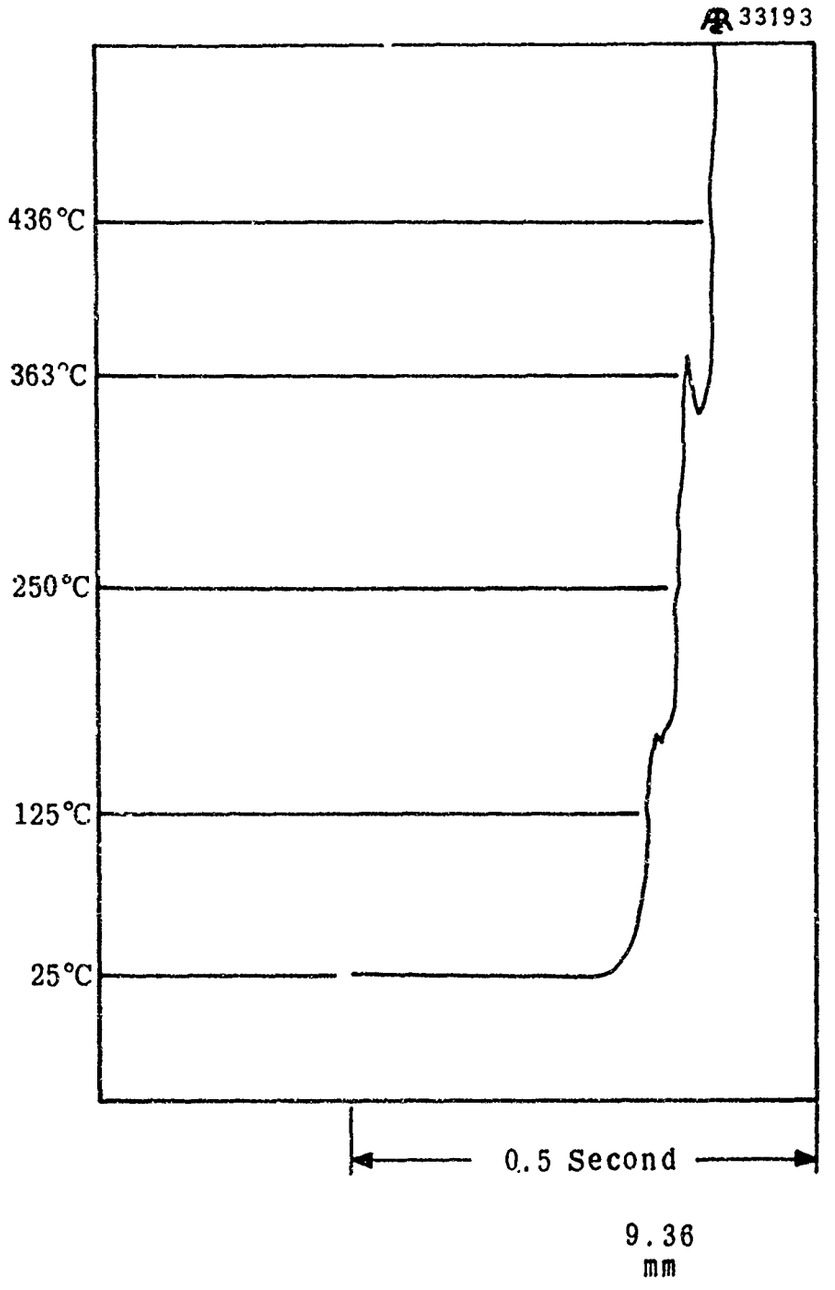


Strand Composition: 94.5% Hydrazine Perchlorate
5% Del-Rin, 0.5% Magnesium Oxide
Density = 1.85 g/cc
Pressure = 0.5 Atmosphere
Deflagration Rate = 0.09 cm/sec

Figure 3. Tracing of Thermocouple Record of Hydrazine Perchlorate Deflagration Wave.



Strand Composition: 94.5% Hydrazine Perchlorate
5% Del-Rin, 0.5% Magnesium Oxide
Density = 1.24 g/cc
Pressure = 1 Atmosphere
Deflagration Rate = 0.30 cm/sec

Figure 4. Tracing of Thermocouple Record of Hydrazine Perchlorate Deflagration Wave.

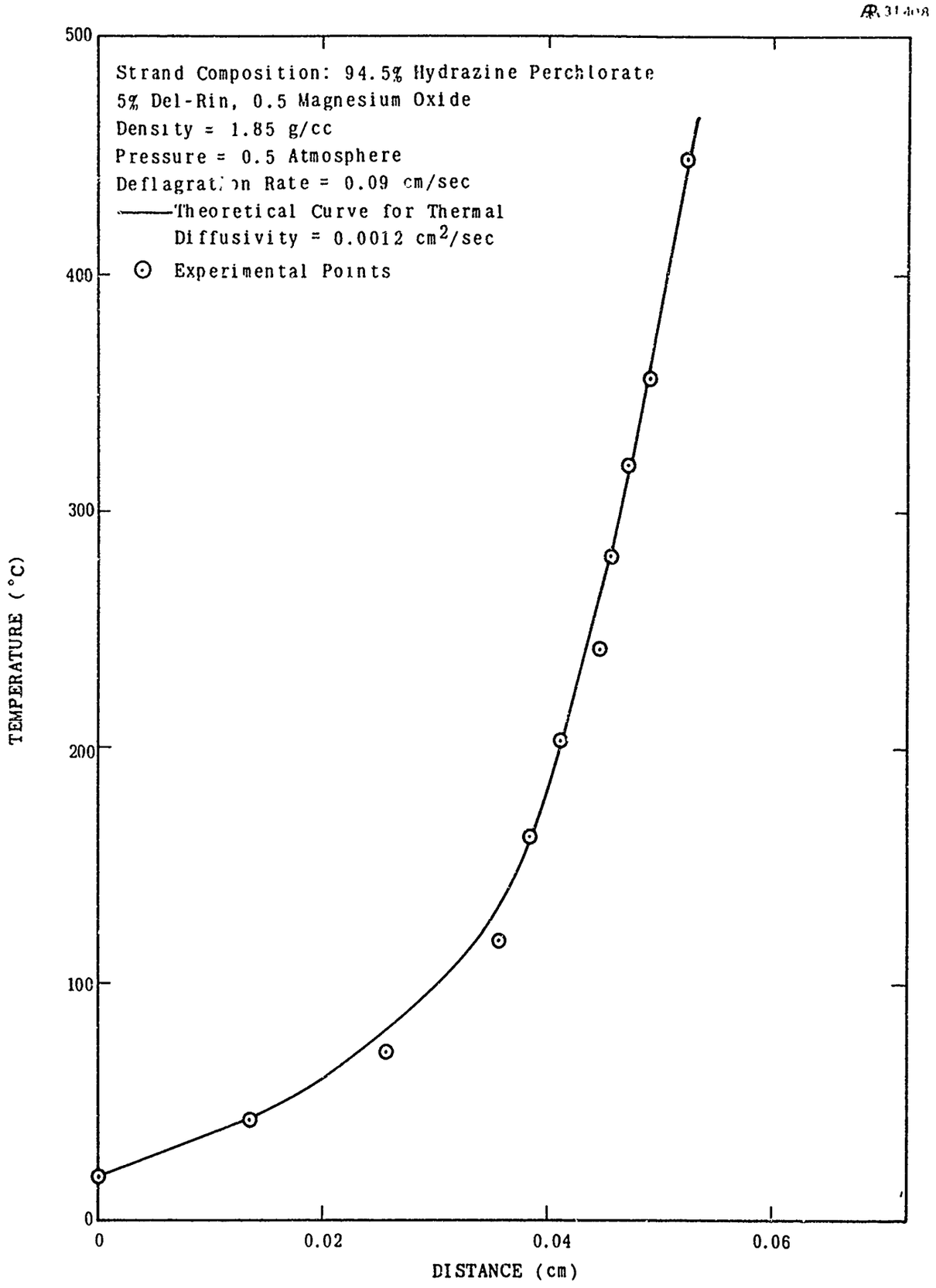


Figure 5. Temperature Profile of a Hydrazine Perchlorate Deflagration Wave.

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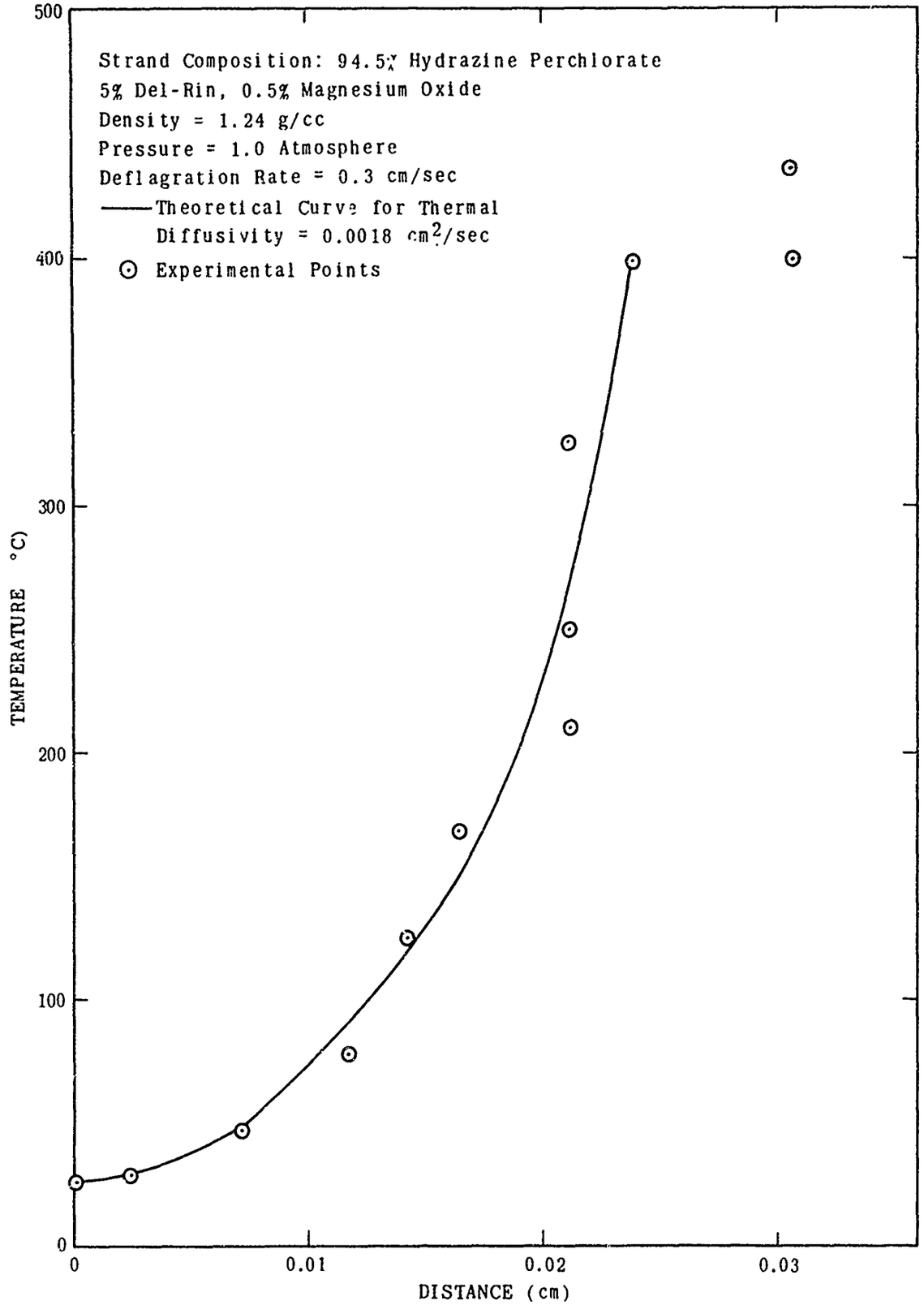


Figure 6. Temperature Profile of a Hydrazine Perchlorate Deflagration Wave.

If $q_c = 0$, the above on integration yields

$$\ln \frac{T_2 - T_u}{T_1 - T_u} = \frac{r}{K} (x_2 - x_1)$$

where $K = \frac{k}{cp}$ = thermal diffusivity, T_2 and T_1 are the temperatures at point x_2 and x_1, and T_u is the ambient temperature.

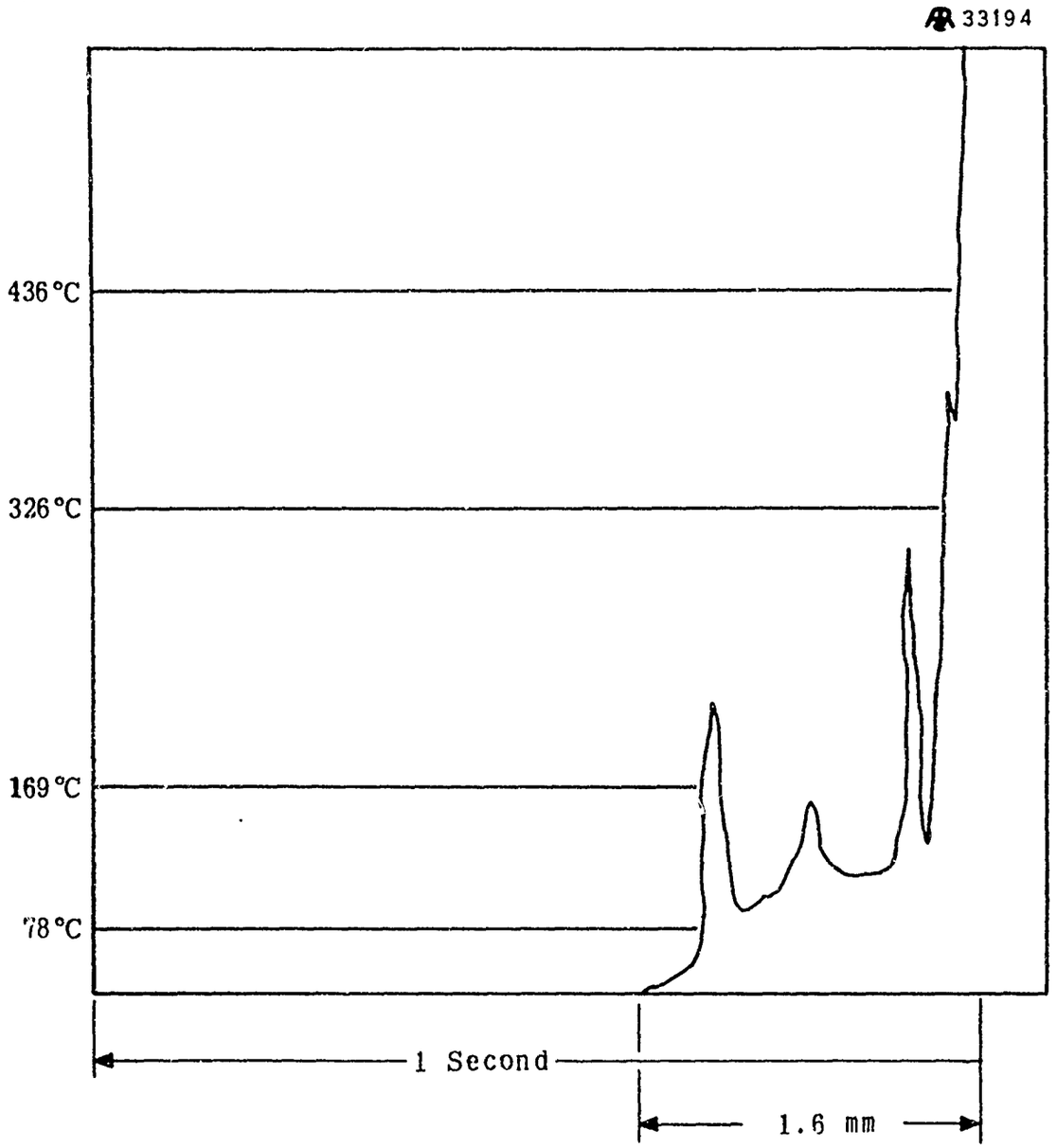
It is possible to evaluate K for the particular experimental data and to fit a T - x curve to the points. As Figs. 5 and 6 show, the values for K that give the best fits are 0.0012 cm^2/sec for the pressed (ρ = 1.85 g/cc) strand and 0.0018 cm^2/sec for the tamped (ρ = 1.24 g/cc) strand. These values can be compared to the value of 0.00285 cm^2/sec which can be calculated for ammonium perchlorate of crystal density, from reported values (13) of heat capacity and thermal conductivity. The values found here thus appear to be of the right order of magnitude.

The curves of Figs. 5 and 6 fit the data fairly well. Thus Fig. 5 gives no indication of heat release in the condensed phase below 450° C. Fig. 6 shows the same result at least to 400° C. It may be further noted that at 0.5 atm, for the pressed strand, Fig. 5, the condensed phase reaction zone was about 0.5 mm thick while at one atmosphere, for the tamped strand, it was about 0.3 mm thick.

Fig. 7 shows the temperature-time records of a hydrazine perchlorate-2% MgO strand at one atmosphere. The distinctive feature is the thickness of the reaction zone ~ 1.6 mm. This may be compared to Fig. 4 for the hydrazine perchlorate-5% Del-Rin-0.5% MgO strand where ambient pressure was also one atmosphere but the zone thickness was about 0.3 mm.

E. Flame Temperature

Thermodynamic calculations of the flame temperature and composition of the deflagration products at various pressures were performed by an IBM-7090 computer program. The results are shown in Table IV. The calculations were made assuming constant-pressure adiabatic



Strand Composition: 98% Hydrazine Perchlorate
2% Magnesium Oxide
Density = 1.05 g/cc
Pressure = 1 Atmosphere
Deflagration Rate = 0.46 cm/sec

Figure 7. Tracing of Thermocouple Record of Hydrazine Perchlorate Deflagration Wave.

combustion to give equilibrium products. As Table IV shows, the flame temperature at 1 atmosphere is 2245.5° K; this is about 800° higher than that for ammonium perchlorate (2). The stoichiometry corresponds closely to

$$N_2H_5ClO_4 \rightarrow N_2 + HCl + 2H_2O + O_2$$

Since it has been found that the self-deflagration of ammonium perchlorate does not lead to the products calculated on the basis of thermodynamic equilibrium, we felt it desirable to measure the flame temperature for hydrazine perchlorate. A flame temperature appreciably different from that calculated would indicate a non-equilibrium distribution of products which would require investigation.

Preliminary experiments were performed in which lengths of one mil platinum wire were stretched through the center of tamped strands of hydrazine perchlorate. Examination of the wire after deflagration showed that the passage of the flame had melted it. The melting point of platinum is 2042° K and the heat loss by radiation was estimated at about 40° K. This placed the flame temperature at somewhere above 2082° K.

Additional data were obtained by the sodium-line reversal method. As described in the literature (14), this method consists in adjusting the brightness of a tungsten ribbon lamp to the brightness of the Na-line emission of the sodium-colored flame gas. The tungsten brightness is controlled by the electric power input and the flame temperature is obtained from a calibration curve of power input versus brightness temperature, furnished by the National Bureau of Standards for the range 1100° - 2300° C. The experiments were made with hydrazine perchlorate strands containing 2% thiourea and 2% sodium chloride. It was found that this amount of sodium chloride was necessary to achieve a sufficient intensity of emission of the sodium D line for these experiments. It may be pointed out that in oxygen-rich, chlorine-containing flames, as this one is, the concentration of sodium atoms is decreased because the equilibrium

$$H + NaCl \rightleftarrows HCl + Na$$

is shifted to the left because the hydrogen atom concentration is so low.

TABLE IV.

HYDRAZINE PERCHLORATE

Constant-pressure adiabatic combustion. Initial temperature 25°C

(ΔH_f = -42.5 kcal/mole)

P (atm) →	1	10	68.05	100
T (°K)	2245.5	2291.6	2318.7	2323.2
Total moles per 100 gm	3.815	3.798	3.787	3.784
Species (Moles/100 gm) ↓				
H	1.008×10^{-3}	2.606×10^{-4}	0.766×10^{-4}	5.949×10^{-5}
O	5.871×10^{-3}	2.456×10^{-3}	1.103×10^{-3}	9.341×10^{-4}
N	0	0	0	0
Cl	0.940×10^{-1}	6.146×10^{-2}	4.112×10^{-2}	3.774×10^{-2}
H_2	5.369×10^{-3}	2.204×10^{-3}	0.982×10^{-3}	8.313×10^{-4}
H_2O	1.526	1.523	1.524	1.525
HCl	0.659	0.688	0.699	0.700
O_2	0.705	0.715	0.719	0.720
OH	4.872×10^{-2}	3.262×10^{-2}	2.231×10^{-2}	2.060×10^{-2}
N_2	0.741	0.740	0.739	0.739
NO	2.606×10^{-2}	2.889×10^{-2}	3.062×10^{-2}	3.090×10^{-2}
NO_2	2.698×10^{-5}	0.898×10^{-4}	2.410×10^{-4}	2.933×10^{-4}
N_2O	0	2.354×10^{-6}	6.512×10^{-6}	0.796×10^{-5}
Cl_2	7.932×10^{-4}	2.588×10^{-3}	6.764×10^{-3}	0.816×10^{-2}

Thermodynamic calculations for the composition containing 2% Thiourea and 2% [illegible]um chloride were made and the theoretical flame temperature was found to be 2224° K. A series of measurements by the sodium line reversal method gave a figure of 2275 ± 50° K for the flame temperature. This is close enough agreement so that we feel that thermodynamic equilibrium is achieved in the flame and the reaction products are as written above. This differs markedly from the results with ammonium perchlorate where a substantial fraction of the nitrogen was present as oxides of nitrogen even at elevated pressures (3).

F. Discussion

The deflagration of hydrazine perchlorate is a process characterized by the formation of a molten zone which is quite turbulent and foamy; it is a very erratic process, particularly for the pure material and it is subject to very potent catalysis by copper chromite and potassium dichromate and to moderate catalysis by magnesium oxide. The process is comparatively reproducible in the presence of small amounts of fuel, and the rate obtained is apparently not dependent on the nature of the fuel but only on the ambient pressure. It is expressible by $\dot{r} = 0.22\ P$ where $\dot{r}$ is in cm/sec and P in atmospheres. This corresponds to a rate, at one atmosphere, some 15 times that calculated by extrapolation for ammonium perchlorate (3) and about twice that found for hydrazine nitroform (15). However the process is unstable at pressures above about 7 atmospheres and steady deflagration cannot be attained above this pressure.

The temperature profile in uncatalyzed strands is such as to indicate little heat production in the condensed phase, and a liquid layer thickness of 0.3 mm at one atmosphere and 0.56 mm at half an atmosphere. This layer is much thicker for magnesium oxide-catalyzed strands.

Finally, from the measured flame temperature, we conclude that thermodynamic equilibrium is attained in the deflagration products.

We ask whether the mechanism of deflagration fits the classification of a vaporization type process like ammonium perchlorate, i.e., where

the material vaporizes without decomposition and exothermic gas-phase reactions occur with resultant heat transfer to the condensed phase. The alternative to a process of this type is one wherein heat production occurs in the molten zone as a result of condensed phase reactions. This latter process appears to be of predominant importance in hydrazine nitroform deflagration.

Here it is of interest to consider the vaporization rate measurements. The data obtained corresponded to the expression

$$\text{Log}_{10} \ (g\sqrt{T}) = 10.0 - \frac{6475}{T}$$

In the temperature profiles of the deflagration experiments both at one atmosphere, Fig. 6, and one-half atmosphere, Fig. 5, temperatures of the order of 450° C were attained. Insertion of this temperature in the above expression yields a vaporization rate of 0.4 gm/cm^2-sec. The deflagration rate found at one atmosphere was 0.36 gm/cm^2-sec while that at half an atmosphere was 0.18 gm/cm^2-sec. The vaporization rate measurements are thus not inconsistent with a vaporization-type mechanism for hydrazine perchlorate deflagration.

If this is considered as one point in favor of a vaporization-type mechanism, a second point in favor of it is the observation that the shape of the temperature profile in the condensed phase was that expected for the case where there is no heat release in the condensed phase. A third point consistent with this picture is the increase of deflagration rate with pressure, a relation that can be explained on the basis that, as the pressure is increased, the exothermic gas-phase reactions occur ever closer to the condensed phase resulting in a higher rate of heat transfer.

The turbulent behavior of the molten zone suggests that the vapor generation is not a smooth process occurring at a uniform rate at every point of the liquid surface, but that it takes place unevenly in the manner of nucleate boiling. This leads to an explanation of the

very erratic nature of the deflagration of pure HP. We note that vapor generation by sublimation such as occurs in ammonium perchlorate deflagration is a smooth process involving continuous detachment of molecules from the surface at a rate depending on the surface temperature only. In this way the smooth deflagration of an AP strand is assured. On the other hand, nucleate boiling is a random process governed by the presence or generation of chance nuclei and the tendency of the liquid to overheat. The latter tendency is presumably very large for a strongly polar liquid such as molten HP. Thus, the HP-deflagration wave is inherently unstable due to fluctuations in the supply of reactant gas to the reaction zone. One estimates that fluctuations causing a diminution of the vapor supply over a period of several microseconds should suffice to reduce the heat feed-back materially and thus to quench the wave in any given small local region. In this situation trace impurities assume a critical role by supplying nucleation centers. It has been noted above that batches of purified material prepared from the same source material by supposedly identical purification processes vary widely in their deflagration behavior, when tested as strands. One batch may not sustain deflagration at all whereas another batch sustains deflagration over some limited but not necessarily reproducible range of pressures and strand temperatures. Systematic studies of HP deflagration are thus limited to strands containing additives of various kinds.

The upper pressure limit of deflagration that has been encountered in the deflagration of "pure" HP at about seven atmospheres may be similarly attributed to the discontinuous nature of the vaporization process. We note that with increasing pressure and correspondingly increasing burning rate the layer width of the molten phase decreases so that the boiling rate becomes increasingly responsive to inhomogeneities in the distribution of nuclei-forming material throughout the HP matrix. This, and perhaps also the consideration that the critical fluctuation period for quenching becomes shorter with increasing burning rate, seems to explain the effect.

As mentioned above, if one tries to force deflagration of pure HP by prolonged application of a heat source the material usually detonates. That is, the layer of molten material that is generated by the heat flux "erupts" after a while and reacts very rapidly, producing a shock that initiates a detonation wave.

IV. HYDRAZINE DIPERCHLORATE STUDIES

A. Experimental

Hydrazine diperchlorate was prepared by the following method:

$$N_2H_4 \cdot H_2O + 2HClO_4 \rightarrow (N_2H_6^{+2})(ClO_4^-)_2 + H_2O$$

A solution of 85% hydrazine hydrate was added to a solution of 72% perchloric acid (a 10 mole per cent excess over that required in the equation). Both solutions had been cooled to 5° C prior to mixing. Water was removed in a flash evaporator until hydrazine diperchlorate began to precipitate and crystallization was permitted to proceed to completion at temperatures slightly below room temperature. The precipitate was collected by vacuum filtration and twice recrystallized from 50% perchloric acid. Hydrazine diperchlorate was then placed in a vacuum drying pistol at 80° C for 18 hours with occasional monitoring until constant weight was reached.

The composition of each batch of HDP varied somewhat; the purity of the material used in all the experiments reported here was 98.6% based on N_2H_4 analysis by the iodometric method. The melting point of the white crystalline solid was 190-192° C.

The hygroscopicity of HDP was measured and found to be significant. For example, at 50 per cent relative humidity, 0.065 moles H_2O were adsorbed per mole powdered HDP in 40 minutes. To avoid any spurious results, handling was carried out as quickly as possible in a controlled-climate room (relative humidity < 20%).

The deflagrations were carried out in a high-pressure optical bomb, with nitrogen as pressurizing gas. The bomb was equipped with fused-silica windows which allowed motion pictures to be taken from which measurements were made. Unless otherwise noted, the HDP was pressed into strands 1-2 cm in length × 8 mm diameter. A pressure of 40,000 psi was applied using a hydraulic press. This yielded strands of 2.11 ± .02 g/cc density in all cases (crystal density of HDP is 2.21 g/cc). The strands were ignited directly with a hot wire, or in some cases the strands were topped with a layer of Arcite (an ammonium perchlorate-polyvinylchloride-plasticizer formulation) which was ignited by the hot wire and in turn ignited the HDP.

The flame temperature of HDP is low enough to allow it to be measured by means of thermocouples. Temperature measurements were made using Chromel-Alumel thermocouples of .001" wire diameter, with a bead diameter of .0025". Finer thermocouples were not necessary in this work. Earlier experiments in the program were performed with Pt/Pt-10% RH thermocouples, but these were found to exhibit catalytic effects at or below the surface of the deflagrating strands, as observed on the motion pictures. Coating the Pt couples with NBS A-418 ceramic coating prevented the catalysis, but reproducible results were difficult to obtain. Uncoated Chromel-Alumel gave rise to no catalytic action and results were highly reproducible. The thermocouples were imbedded in the strands before pressing and were visible on the pictures of the deflagrations. The voltage output was measured by means of a Honeywell Visicorder Oscillograph.

The strands for both the deflagration-rate measurements and the temperature measurements were fitted into tight-fitting Pyrex tubes. This inhibited side burning and insured uniform regression of the strand surface. No attempt was made to control particle size in any of the experiments.

B. Results

1. Deflagration Rate and Effect of Catalysts

The deflagration is a non-luminous process and is characterized by a liquid layer whose thickness decreases with increasing pressure.

There is considerable foaming and bubbling in the liquid. At pressures above about 30 atm the bubbling is no longer observable. The liquid layer can still be seen on the motion pictures up to pressures approaching 100 atm, but above this pressure it cannot be determined definitely whether a liquid layer still exists. At the low pressures (below 20-25 atm), a "pulsing" of the heated condensed phase is very prominent, i.e., the molten foam layer on top of the strand appears to expand and then suddenly contract, as if gas is being generated below the surface, acting to expand the foam, which upon release allows the surface to regress.

The linear deflagration rate as a function of pressure is shown in Fig. 8 and the data tabulated in Table V. The mass deflagration rate is similar since the density of the strands was so carefully controlled. The data obtained do not represent the deflagration limits of HDP. The upper pressure limit was set by the capacity of the apparatus. The lowest points shown (6 atm) are those where the strands could be ignited and were consumed reproducibly. Occasionally in quenching experiments (see below), strands were consumed partially or totally, even at 1 atm. The quality control of the HDP was found to be very important in obtaining reproducible rates. Small changes in composition (of the order of tenths of a per cent in assay) caused the rates to vary by as much as a factor or two.

In Figure 9, the data are shown on a log-log-plot. The lines were drawn visually and the Vieille's law expressions ($r = bP^n$) were computed. The pressure exponent is seen to change drastically from low to high pressure. This fact will be discussed later, but it is relevant to point out that as pressure increases the bubbles in the liquid become smaller in size and much greater in number. This is accompanied by an increase in frequency of the pulsing, which disappears altogether by $\sim$ 20 atm. These observations permit some understanding of why the pressure exponent is greater than unity in the low pressure range.

The effects of catalysts on the deflagration rate were examined and the results are presented in Table VI. The density was 2.1 $\pm$ .1 g/cc for all strands. The particular choice of catalysts was made partly to provide some basis for comparison with hydrazine perchlorate and ammonium

TABLE V

Deflagration Rate Data for HDP

$\dot{r}$ (cm/sec)	P atm
.03	6.1
.02	6.1
.05	11.2
.145	21.4
.21	28.2
.34	35.4
.44	42.2
.47	49.4
.43	49.0
.56	56.1
.62	62.9
.75	70.1
.85	90.7
.94	111
1.10	135
1.26	216
1.27	265
1.4	328

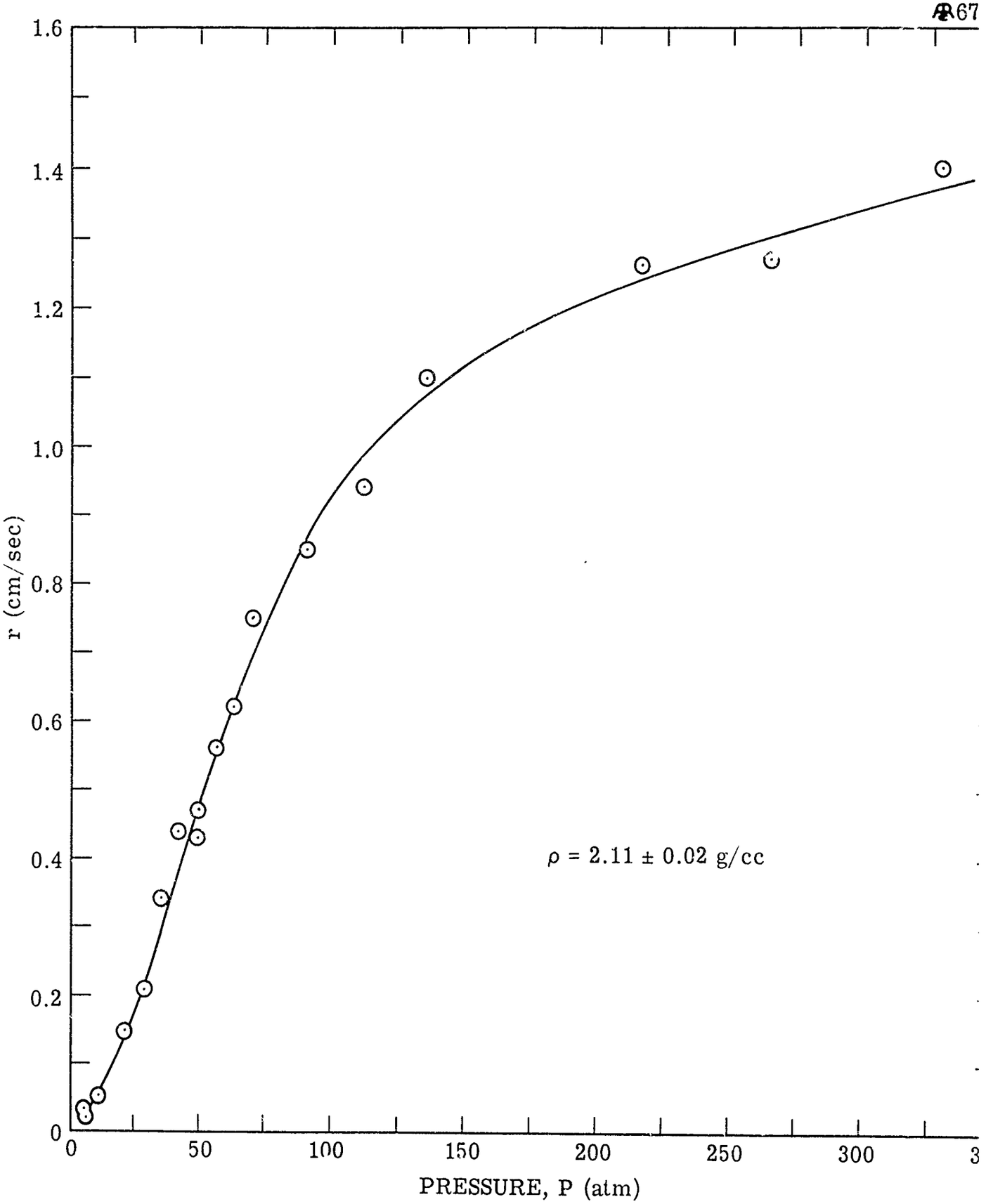


Figure 8. Linear Self-deflagration Rate of Hydrazine Diperchlorate as a Function of Pressure.

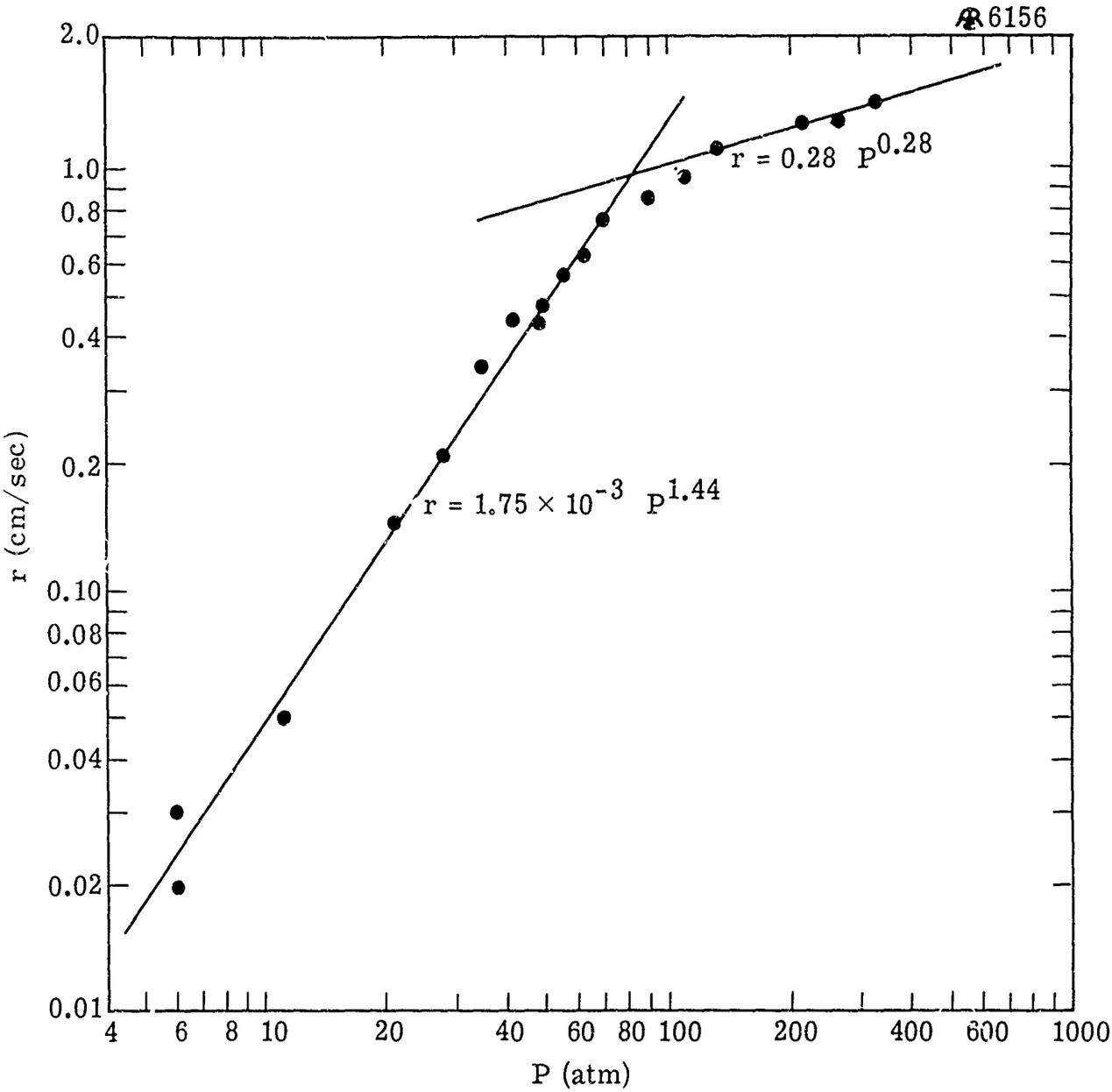


Figure 9. Log-Log Plot of Linear Self-Deflagration Rate of HDP Versus Pressure.

TABLE VI

THE EFFECTS OF CATALYSTS ON THE DEFLAGRATION OF HYDRAZINE DIPERCHLORATE

Catalyst	Weight%	Pressure (atm)	Linear Rate (cm/sec)
Pure HDP	0.00	1	0.002 (a)
$CuCrO_2$	0.5	1	incomplete
	1.0	1	0.081
	2.0	1	0.12
	5.0	1	0.25
	10.0	1	0.24
	2.0	40	too fast (b)
	2.0	70	to measure (b)
$Na_2Fe(CN)_5NO \cdot 2H_2O$	0.5	1	0.037
	1.0	1	0.052
	5.0	1	0.127
MgO	2.0	1	incomplete
	5.0	1	0.011
	2.0	8	irreproducible
	2.0	11	0.16

(a) Extrapolated from data of Figure 9.

(b) In these experiments the strands were consumed between two frames of the motion pictures (64 frames/sec). It is not known however whether a true deflagration occurred.

perchlorate deflagrations. Sodium nitroprusside was examined because of its reported catalytic activity in liquid bipropellants containing hydrazine (4). The following observations are made on the catalyzed deflagrations.

Magnesium oxide causes an increase in rate of approximately a factor of 3 at the 2% level. Motion pictures show that the deflagration proceeds with a liquid layer with foaming, bubbling, and pulsing. These effects are present but on the wane at 1 atm with 5% MgO and at 11 atm with 2% MgO.

Copper chromite increases the deflagration rate at low pressure by more than an order of magnitude at concentrations as low as 1% by weight. Strands with 1% $CuCrO_2$ exhibited a bubbling liquid layer but no pulsing. Only a hint of this bubbling remained at the 5% level. The effect of sodium nitroprusside on the deflagration is intermediate in magnitude to that of MgO and $CuCrO_2$, and no unusual behavior was observed.

By way of comparison of the effects of catalysts on ammonium perchlorate, HP, and HDP, it can be said that no extraordinary differences were observed. $CuCrO_2$ has a strong catalytic effect on all three monopropellants, being strongest in the HDP case. An additional comparison is of interest: HDP deflagrates at approximately the same rate as ammonium perchlorate (above 22 atm)(2), but hydrazine perchlorate is over an order of magnitude faster. Parenthetically it should be noted that when fuel-type additives, viz., Del-Rin*, Thiourea and Naphthalene, were added to HDP they were found to be incompatible, as evidenced by swelling and foaming of the mixtures.

The motion pictures of the deflagrations clearly showed the liquid layer at pressures of about 30 atm and below, and less clearly at higher pressures. The liquid would wet the inside of the Pyrex tubes containing the strands, altering the index of refraction change and causing the inside diameter of the tube to seemingly disappear. This afforded a means of measuring the thickness of the liquid layer. These measurements are presented in Figure 10 for strands burning at various pressures. Since no particular significance could be attached to these data, they are offered without comment.

* A polyformaldehyde supplied by [illegible]

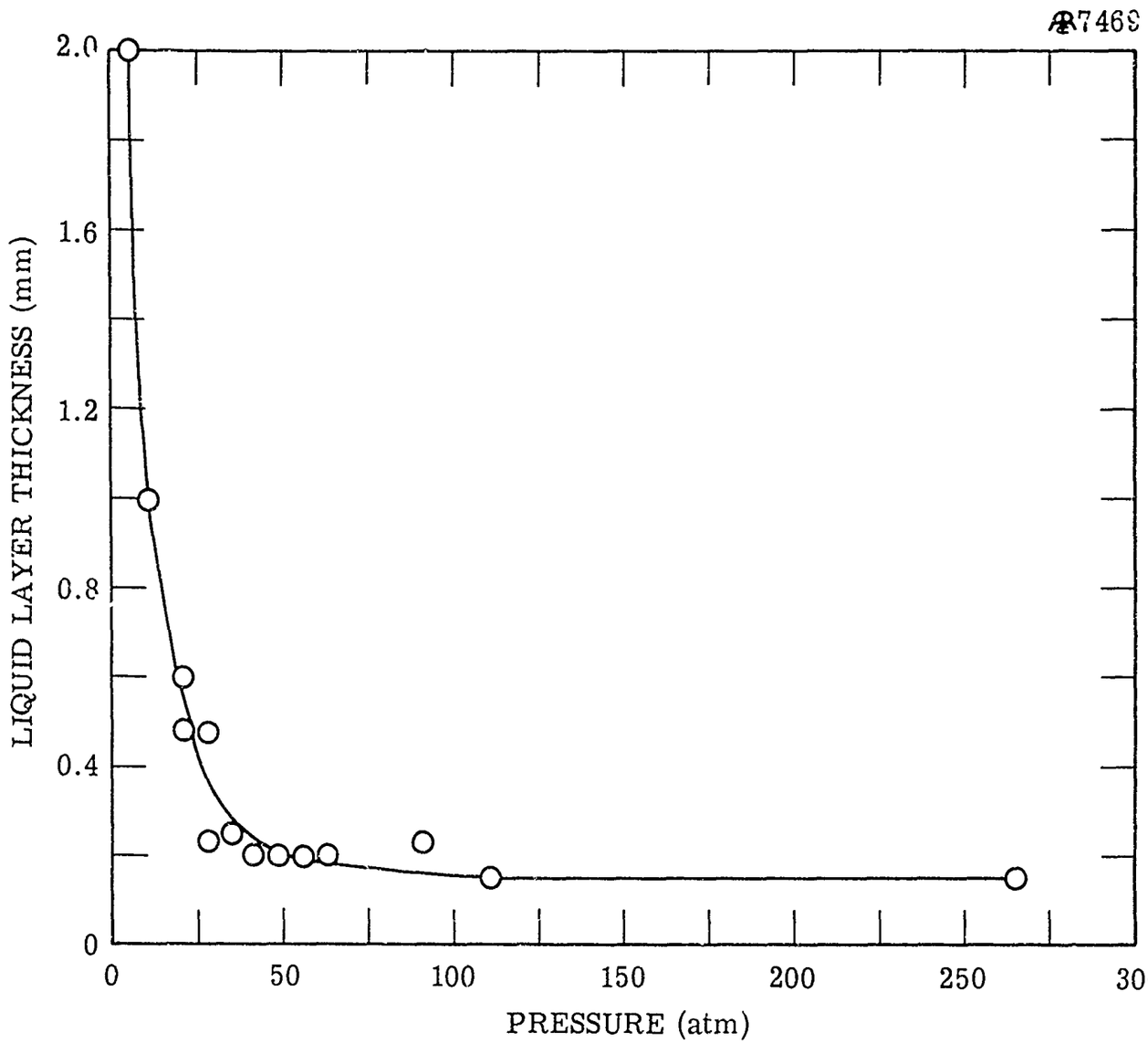


Figure 10. Liquid Layer Thickness as a Function of Pressure for HDP Deflagrating Strands.

469

2. Flame Temperature

The theoretical adiabatic flame temperature of HDP was computed to be 1593, 1600, and 1604°K at 1, 10 and 100 atm, respectively. This computation was performed on an IBM 7090 computer; it is for an initial temperature of 25°C and yielded a reaction stoichiometry very close to

$$N_2H_6(ClO_4)_2 \rightarrow N_2 + 2H_2O + 3\,O_2 + 2HCl$$

For this calculation, the standard heat of formation of HDP was taken as 71.8 kcal/mole, estimated from the following data: The heats of formation of the aqueous ions $N_2H_6^{++}$ and ClO_4^- are -4 and -31.4 kcal/mole, respectively (NBS Circular 500); the heat of solution of HDP was estimated at +5 kcal/mole, based on the data for analogous hydrazine and perchlorate compounds. The last value is probably the most uncertain, and this by an estimated ± 2 kcal/mole. This corresponds to an uncertainty in flame temperature of approximately ± 26°K.

The experimentally determined flame temperatures are tabulated in Table VII and shown as a function of pressure in Figure 11. The observed temperatures are lower than the true gas temperature because of radiation loss of the thermocouples. The corrections to be applied were calculated using the formula

300

$$T_g - T_c = \frac{\epsilon \sigma d}{\lambda}\,\frac{(T_c^4 - T_w^4)}{Nu}$$

where

T_g = true gas temperature
T_c = thermocouple temperature observed
T_w = temperature of surface adsorbing radiation
σ = Stefan-Boltzmann constant
ϵ = emissivity of thermocouple
d = bead diameter
λ = thermal conductivity coefficient of gas
Nu = Nusselt number

TABLE VII

FLAME TEMPERATURE MEASUREMENTS IN HYDRAZINE DIPERCHLORATE DEFLAGRATION USING FINE CHROMEL-ALUMEL THERMOCOUPLES

Pressure	28 atm	55 atm	103 atm
T observed (°K)	1355	1490	1550
	1355	1465	1545
	1325	1475	
	1370	1510	
	1310	1455	
	1365	1465	
	1365		
	1325		
Average	1345 ± 20	1475 ± 15	1550 ± 5
Radiation Correction (°K)	40 ± 15	45 ± 20	45 ± 20
Flame Temperature (°K)	1385 ± 35	1520 ± 35	1595 ± 25

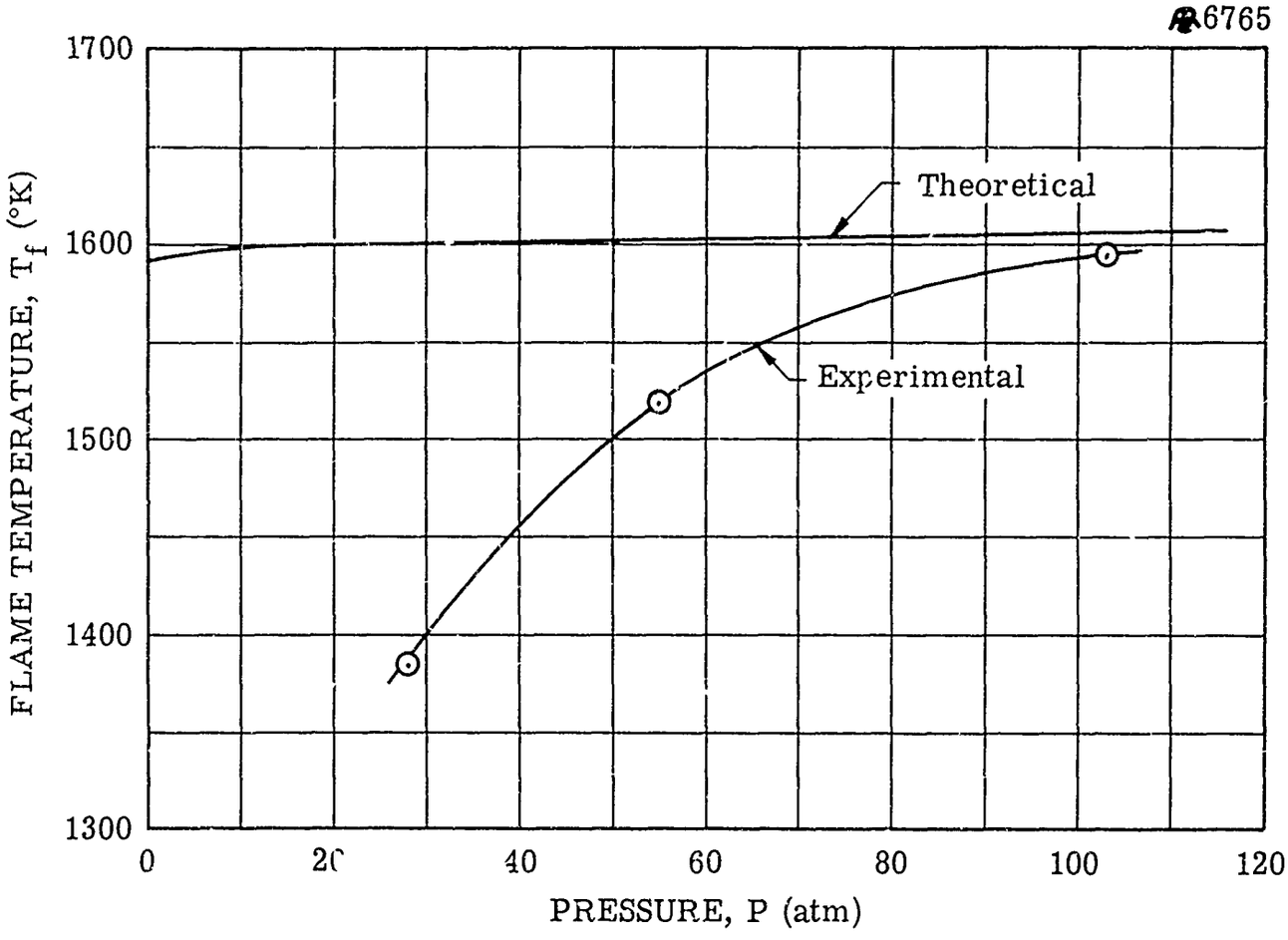


Figure 11. Flame Temperatures of HDP as a Function of Pressure.

The emissivity of Ch-Al is 0.36 for the unoxidized metal and 0.87 for the oxidized (16); λ was calculated by the method of Andrussow (17) using the theoretical gas composition; the Nusselt Number was obtained from the Reynolds number (18). The corrections are shown in Table VII; they are not large but not negligible. Since the degree of surface oxidation of the thermocouples was not known and no attempt was made to control it, the corrections applied were averages for the oxidized and unoxidized metal. This introduced only a small uncertainty.

The nature of the deflagration process below $\sim$ 25 atm is such that it does not lend itself to a measurement of the flame temperature. This point will be discussed subsequently, as will the falling off of the flame temperature below approximately 100 atm.

3. Temperature Profile

In Figure 12, tracings of the thermocouple-output records are shown for deflagrations at 10, 15 and 21 atm. As the pressure increases, the profile gradually takes on the shape of a normal flame profile. The pulsing, noted earlier, gives rise to the erratic temperature fluctuations, which smooth out and eventually disappear at higher pressures. The temperature at which pulsing sets in was not too reproducible, sometimes occurring at or near the melting point (191°C), but other times in the neighborhood of 140°C (the melting point of hydrazine perchlorate is 141°C).

In Figure 13a is presented a thermocouple-output record for a deflagration at 18 atm, in which the temperature profile through the condensed phase was obtained with higher sensitivity. The temperature-distance plot constructed from this record is shown in Figure 13b. The one-dimensional steady-state heat-balance equation which describes the temperature through a combustion wave is

$$\frac{d}{dx}\left[\lambda \frac{dT}{dx}\right] - C_p \rho r \frac{dT}{dx} + Q(x) = 0 \qquad (1)$$

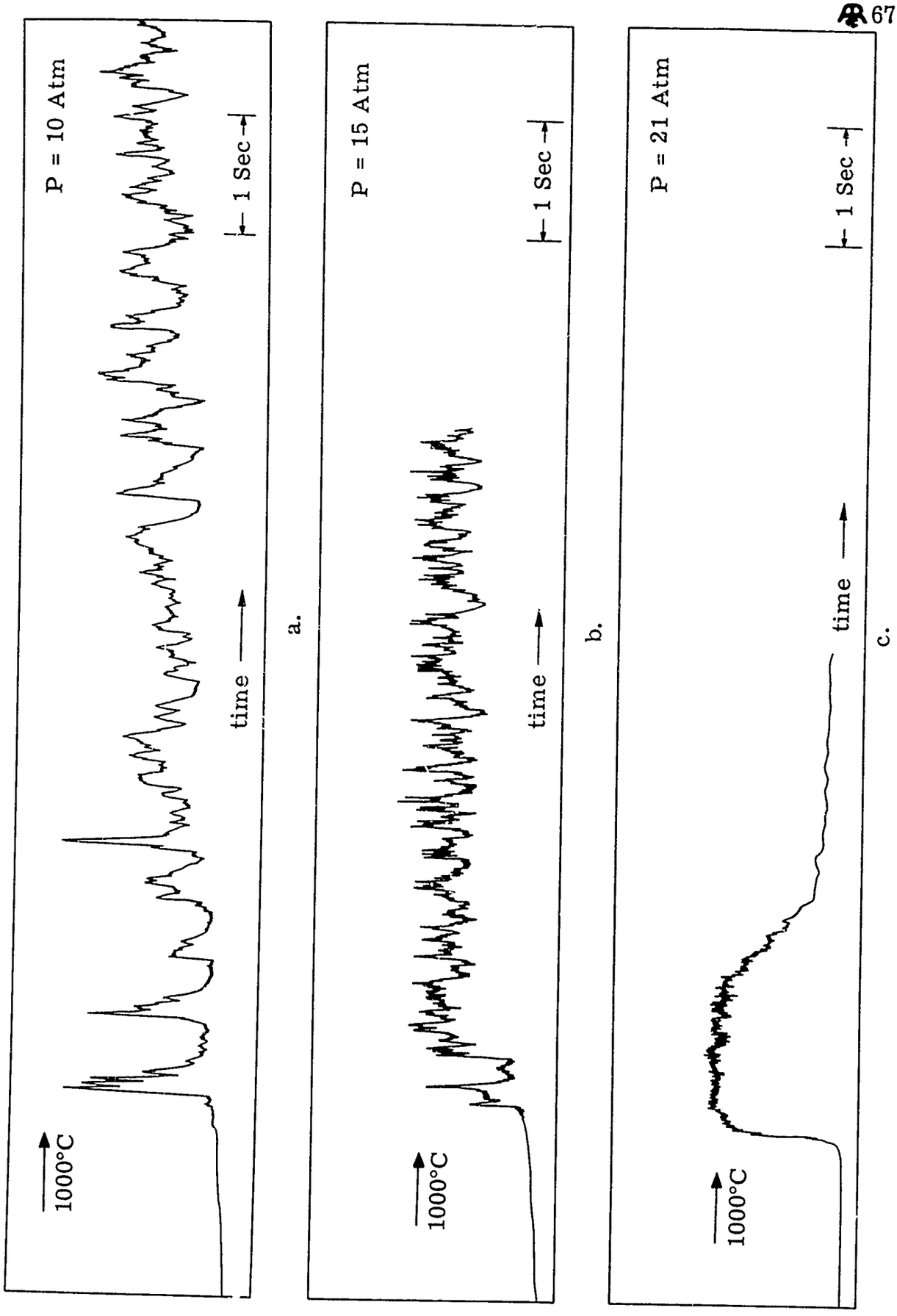


Figure 12. Tracings of Thermocouple - Output Records for HDP Deflagrations at Low Pressure.

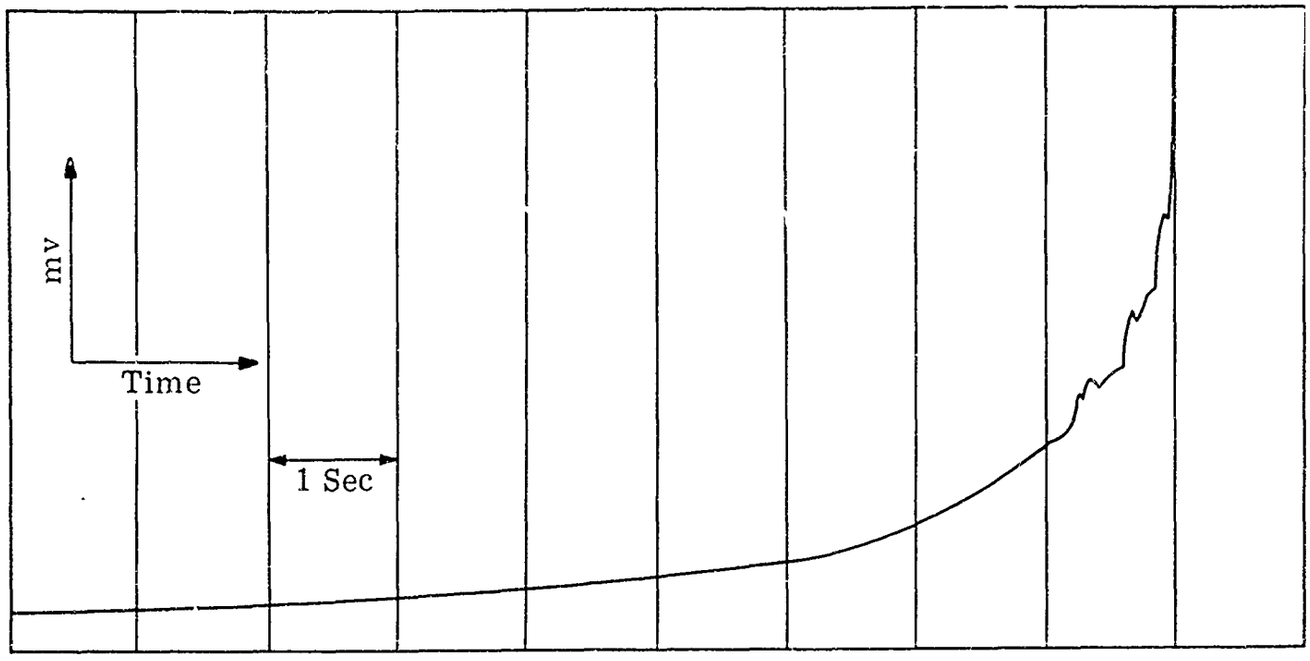


Figure 13a. Tracing of Thermocouple - Output Record Through Preheat Zone in HDP Deflagration.

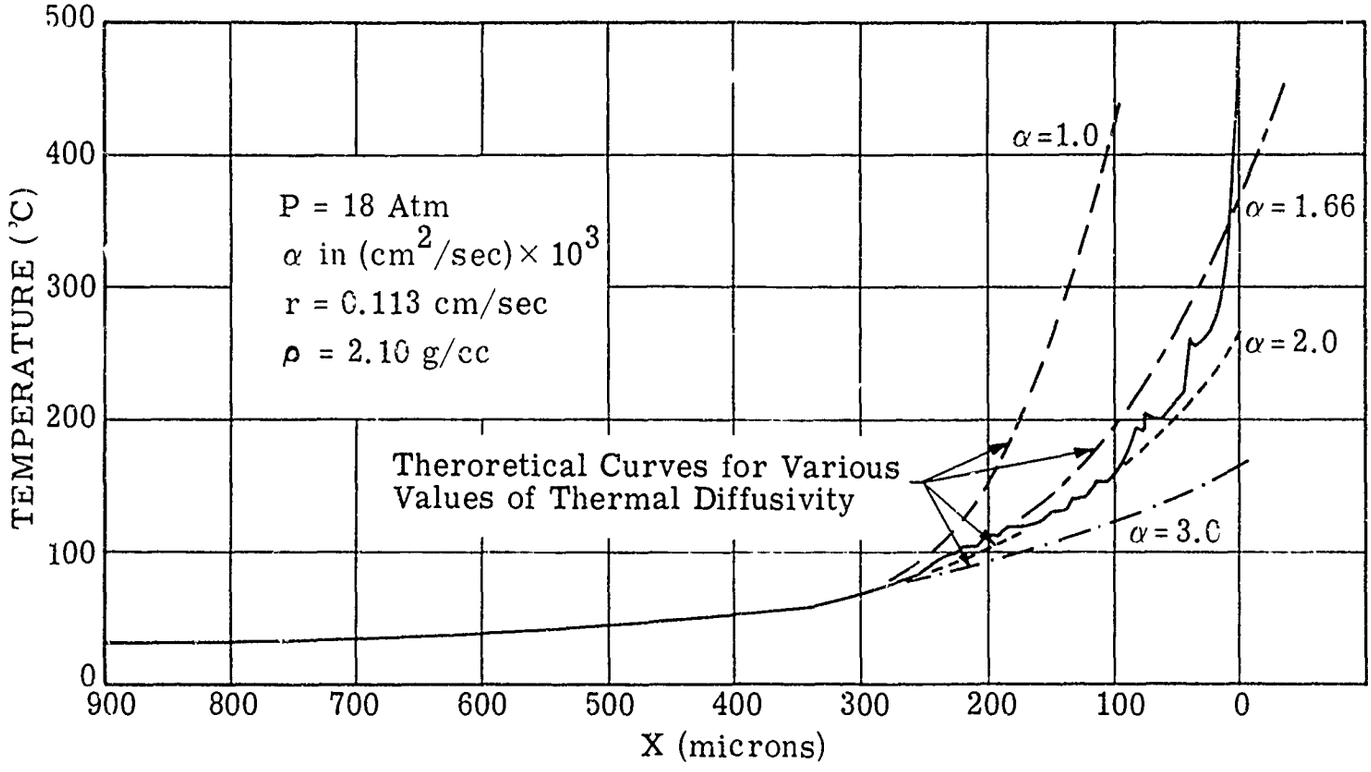


Figure 13b. Temperature Profile Through HDP Deflagration Wave Obtained from above Record.

764

where

λ = coefficient of thermal conductivity
C_p = specific heat
ρ = density
r = linear deflagration rate
$Q(x)$ = heat produced at point x due to chemical reaction

If $Q(x)$ is set equal to zero, and λ, C_p, and ρ are taken as constant, the above equation integrates to

$$T_1 - T_u = (T_2 - T_u) \exp \frac{r}{\alpha} (x_1 - x_2)$$

where

T_u = ambient temperature ($x = -\infty$)
T_1, T_2 = temperatures at points x_1, x_2
$\alpha = \lambda / C_p \rho$ (thermal diffusivity)

In Figure 13b, the theoretical equation is plotted for various values of thermal diffusivity. The shape of the profile is seen to be a very sensitive function of α. By invoking a small decrease in α with increasing T, it is possible to reproduce the general path of the temperature. The thermal diffusivity of ammonium perchlorate has been reported to decrease from 2.17×10^{-3} cm^2/sec at 50°C to 1.35×10^{-3} at 240°C (19). A change of the same magnitude for HDP is indicated by the data in Figure 13. It is clear that treating α as constant, as is often done when examining temperature profiles of the preheat region of a deflagration wave, can be a hazardous assumption.

The irregular temperature deviations from a smooth curve, seen in the profile, are easily understood to be heat surges seen by the thermocouple. Random pockets of hot gas and molten liquid of varying heat content must be intermittantly coming into contact with the thermocouple bead. The liquid zone is an agglomeration of heat sinks and sources of varying size and degree. So long as the bead is commensurate in size with these, the general

shape of the profile in the preheat region is expected to resemble that predicted by equation (1). This is seen (Figure 12) to fail at lower pressures.

4. Quenching

The quenching experiments fall into two groups: (1) those in which deflagrating strands were suddenly extinguished by venting the pressure in the bomb to ambient, and (2) those in which HDP, packed into capillary Pyrex tubing, was ignited in order to determine the quenching diameter as a function of pressure.

In the venting experiments, extinguished strands were recovered and the fused layer on top was scraped off and analyzed. It was found to contain considerable quantities of NH_4ClO_4. During these and other deflagrations at low pressures, a white solid was observed to have been thrown out of the molten phase during pulsing and to have collected on the walls of the glass tubes. This material was recovered and analyzed and was found to be entirely ammonium perchlorate. These analyses were performed by infrared spectroscopy, with synthetic mixtures of HDP and NH_4ClO_4 serving as standards for semi-quantitative estimates.

In the second type of quenching experiments, deflagration-rate measurements were made on HDP packed (density = 1.4 g/cc) into 1.15 mm i.d. Pyrex tubes. At 70, 40 and 28 atm the deflagrations were identical in appearance to those observed in the 8 mm tubes, and the mass rates were the same. At the two lower pressures, an acidic liquid was found in the tubes after the runs. From the motion pictures, this liquid could be seen to be condensing at the top of the tube during the deflagration. Another series of experiments between 18 and 23 atm was carried out in the 1.15 mm tubes. At the lower end of this pressure range, deflagration never took place; at the upper end, deflagration commenced and then ceased before all the HDP was consumed. However, it was clear that the condensed liquid mentioned above ran down the tube walls and extinguished the material.

No information on quenching distance could be obtained due to the nature of the combustion process at the lower pressures, and it would not be feasible to measure quenching diameters at high pressures because of the fineness of the capillaries that would be required. The experiments did yield valuable qualitative observations on the deflagration and showed that the data of Figure 8 are independent of the diameter of the tubes used.

5. Thermal Decomposition

The results of these studies will be presented in summary form since the decomposition has been reported (20) and our work is in substantial agreement.

Small quantities of HDP, of the order of 50 mg., were heated in a 7 mm o.d. Pyrex reaction tube which was inserted in a well in an electrically heated block. Experiments were carried out from 174 to 293°C. The increase in pressure with time was followed manometrically, and the gases and solid residues were analyzed. The stoichiometry was found experimentally to be

$$N_2H_6(ClO_4)_2 \rightarrow .5\ NH_4ClO_4 + .74\ N_2 + .20\ O_2 + .29\ HCl + 0.06\ N_2O$$
$$+ .03\ H_2 + 1.2\ HClO_4 + .7\ H_2O$$

The last two coefficients were not gotten directly but were chosen to yield the best mass balance.

One important difference was found between the present study and that of Grelecki and Cruice. They observed that HDP decomposed very slowly for periods of 9 to 77 hours (at 120 to 150°C), then suddenly the reaction accelerated and went to completion (within seconds). Their study was carried out in a Sickle Gage apparatus made entirely of glass, thus allowing the entire apparatus to be kept at reaction temperature. They found that small amounts of $HClO_4$ greatly decreased the time to acceleration, and small amounts of NH_3 gas greatly increased it. The

initial step in the decomposition was verified as

$$N_2H_6(ClO_4)_2 \rightarrow N_2H_5ClO_4 + HClO_4 \quad ,$$

the heat of dissociation being 37 kcal/mole.

In the present experiments, a sudden acceleratory effect was not observed, rather the pressure-time curves were found to rise gradually if not too reproducibly, to some final level. In all the experiments, droplets of an acidic liquid were observed to form on the tube walls above the heated portion of the apparatus. Thus, the attack by $HClO_4$ and/or its degradation products on the solid substrate plays a key role in the decomposition.

6. Chemical Tests

The deflagration of solids involves the gasification of condense material into an exothermic reaction zone. This gasification process can occur by one of three modes (21): sublimation, as with ammonium perchlora nucleate boiling, as with hydrazine perchlorate; or chemical attack, as with hydrazine nitroform (15) and hydrazine diperchlorate. When the gasification step occurs by chemical attack, it is necessary to elucidate the nature of the reactions if the chemical mechanism of the deflagration is to be understood. This was done in the case of $N_2H_5C(NO_2)_3$ (15), where it was found that a primary decomposition product is nitrogen dioxid The NO_2 in turn was found to attack the solid, causing the release of more NO_2. Thus the decomposition is self-acceleratory and explosive, unless the NO_2 is allowed to escape. When a stream of NO_2 gas was passed over hydrazine nitroform at 25° C the solid burst into flame. Hydrazine perchlorate likewise burst into flame when NO_2 was passed over it. An attempt was made to determine which chemical species is responsible for the condensed-phase reactions observed with HDP. It seemed likely that ClO_2 played the same role in HDP decomposition and gasification as NO_2 played in hydrazine nitroform.

Chlorine dioxide was generated by mixing potassium chlorate with moist oxalic acid and warming to about 90° C according to the following equ

$$2KClO_3 + 2\,H_2C_2O_4 \xrightarrow[\Delta]{H_2O} K_2C_2O_4 + 2\,H_2O + 2\,CO_2 + 2\,ClO_2$$

The reaction was carried out under a very slow flow of nitrogen at atmospheric pressure. When ClO_2 was produced, as evidenced by its intense yellow color, it flowed through a Pyrex train containing a section packed with Drierite to remove H_2O and then through a 10 mm i.d. U tube. HP and HDP were alternately placed in the U tube. No visible reaction was observed as the ClO_2 passed over these oxidizers at 25° C and at 100° C. In all experiments the HP and HDP were recovered and analyzed by infrared spectroscopy. No change from the starting materials could be detected and no evidence of NH_4ClO_4 formation was present.

A number of other results were found in the course of these experiments which are here reported. In control experiments, the ClO_2 passed through the U tube at 25° C unchanged. When the U tube was at 100° C, however, the ClO_2 exploded as it passed through. There were indications that if the ClO_2 vapor was relatively dilute (faint yellow) it exploded immediately upon coming into the 100° C section of the U tube, whereas more dense ClO_2 vapor (intense yellow) passed entirely through the U tube for several seconds before exploding. Packing the U tube with Pyrex wool prevented the explosion at 100° C. This procedure was followed when HP and HDP were being tested. These observations suggest that a chain-branching mechanism may be responsible for ClO_2 explosions.

The reaction of ClO_2 with N_2H_4 was also investigated. Approximately 0.1 cc of liquid N_2H_4 were placed in the U tube and ClO_2 gas was permitted to flow into it at 25° C. As the first ClO_2 vapor (very faint yellow) entered the U tube, heavy white fumes appeared above the N_2H_4 and on the exit side of the U tube. When the yellow vapors became moderate in intensity, the ClO_2 exploded and flashed back into the generator. At this point, white fumes filled the U tube and a white solid with brownish streaks remained in the U tube. This solid was analyzed by infrared spectroscopy and found not to contain AP, HP or HDP. It exhibited a broad IR adsorption from about 3500 to 2200 cm^{-1}. Other well-defined bands appeared

at 2050, 1930, 1810, 1570, 1490, 1400, 1235, 1075 and 955 cm^{-1}. The bands observed are characteristic of N-H-containing cations and $CO_3^{=}$, NO_3^{-}, ClO_3^{-} and ClO_4^{-} anions. Small amounts of NH_4Cl and NH_4NO_3 could have been present.

7. Deflagration Experiments in Fuel Gas Streams

At the Tenth Combustion Symposium (22), experiments were reported in which ammonium perchlorate spheres (of 6-7 mm diameter) at atmospheric pressure were supported on a wire grid located at the center of a duct, a fuel gas caused to flow through the duct, and the spheres ignited by a hot wire. The fuel gases used were propane, ammonia, hydrogen, and hydrogen diluted with nitrogen. It was found that ammonium perchlorate would undergo steady deflagration under these conditions while, if an inert gas replaced the fuel gas, deflagration did not occur. The data obtained obeyed various rate laws depending on the fuel.

The form of the rate law so obtained should be informative as to the factors governing deflagration. Accordingly we have carried out a number of experiments using this technique in an apparatus as described above. The resultant events were recorded on motion picture film. Experiments have been performed with ammonium perchlorate, hydrazine perchlorate and hydrazine diperchlorate.

a. Ammonium Perchlorate

Our interest in studying the deflagration of ammonium perchlor by this technique was to allow a comparison of our results with those of Barrere and Nadaud (22) and to allow the comparison of ammonium perchlorate with hydrazine perchlorate and hydrazine diperchlorate. It was found that smooth deflagration could be attained in the flow rate range of 5.75-23.3 cm/sec. The limiting flow rates for deflagration were not investigated so that it may be that deflagration can occur outside the above limits.

Subsequent experiments were performed on pressed 8 mm diameter spheres of ammonium perchlorate, prepared using a spherical mold. When the sphere was ignited, it was possible to observe a first stage during which

ignition spread over the sphere surface from the point at which the hot wire touched it. Thereafter the sphere deflagrated smoothly. However a major source of difficulty was encountered in the ammonium perchlorate experiments in that after about half of the sphere had been consumed, it would split into two or more irregularly-shaped fragments. The fragments assumed a spherical shape after sufficient further deflagration had occurred but were then quite small. This behavior occurred with all the fuel gases used, i.e., methane, propane and hydrogen.

The results for methane and propane have been plotted using the function $D^2 = D_b^2 - kt$ where D and D_b are the horizontal diameters at time t and at zero time respectively, t is time in seconds, and k is a proportionality constant which is a measure of the deflagration rate. Barrere and Nadaud found that their data obeyed this expression for propane and ammonia as fuels.

The type of data obtained in our experiments is illustrated by Figure 14 where our best results for ammonium perchlorate, hydrazine perchlorate, and hydrazine diperchlorate are shown. As Figure 14 shows, the data points are quite scattered but are roughly linear. The results obtained with ammonium perchlorate are tabulated in Table VIII below along with results for hydrazine perchlorate and hydrazine diperchlorate.

b. Hydrazine Perchlorate

Experiments were performed with hydrazine perchlorate spheres in streams of methane and propane. Here the spread of ignition over the sphere's surface was evidenced by the formation of a molten layer over the surface. The deflagration rate was many times faster than that for ammonium perchlorate. When the data were plotted in the same way as for ammonium perchlorate, slopes of the order of 5-10 times those obtained for ammonium perchlorate were found (see Figure 14). Deflagration of hydrazine perchlorate exhibited certain peculiarities. On the one hand it was observed that the hot ignition wire remained in contact with the hydrazine perchlorate

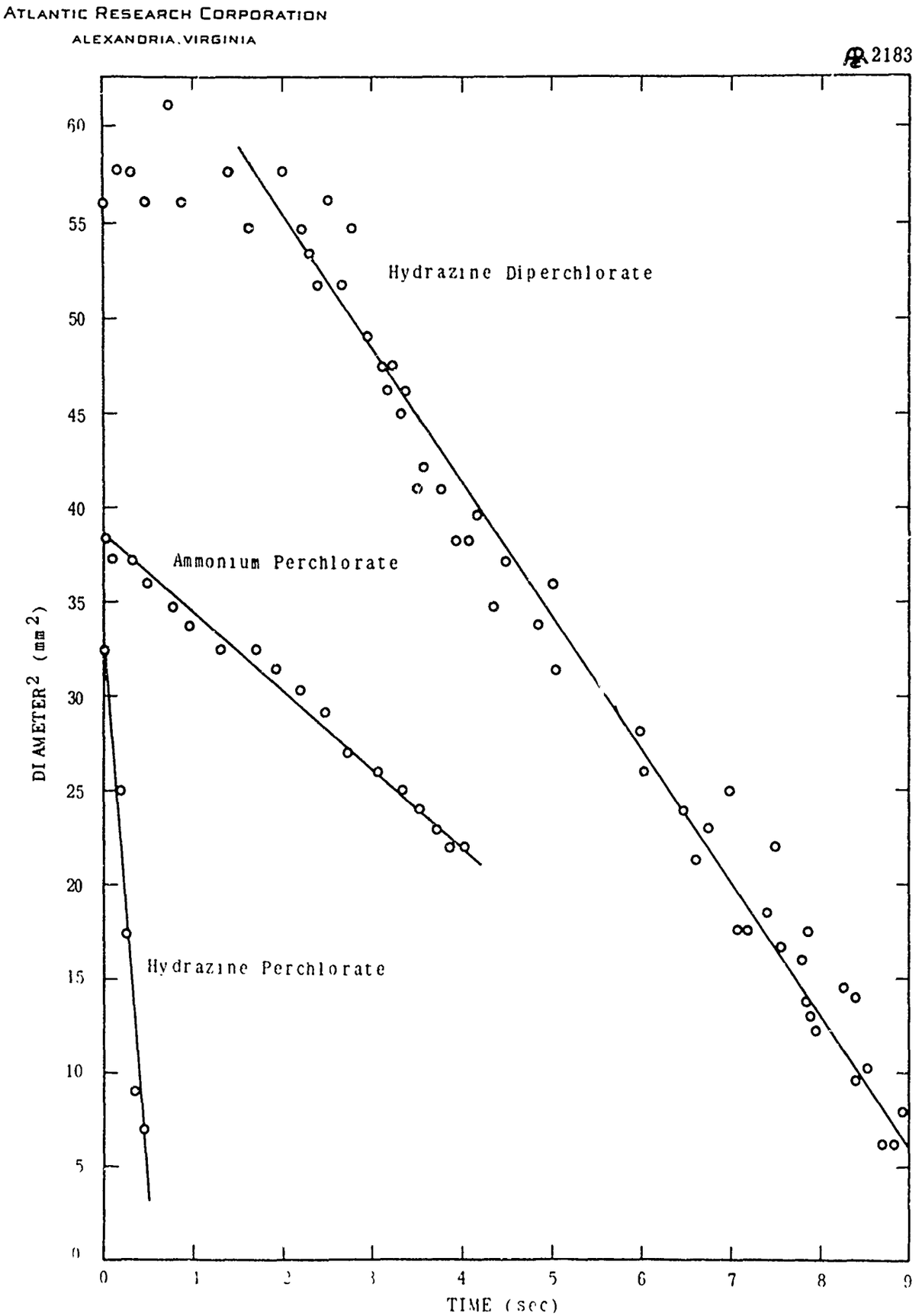


Figure 14. Deflagration Rates in a Methane Stream (Flow Rate = 15.5 cm/sec).

sphere for periods as long as one minute with no perceptibel effect other than melting of hydrazine perchlorate at the point of contact. Ignition then occurred followed by very rapid deflagration. Another phenomenon that was noted with hydrazine perchlorate and was even more prominent with hydrazine diperchlorate was the occurrence of pulsing, explained earlier. The deflagration process was actually a series of such pulses. This resulted in very erratic plots of D^2 vs t.

c. Hydrazine Diperchlorate

Experiments with hydrazine diperchlorate have been performed with methane, propane and hydrogen fuel gases. Deflagration rates were of the same general magnitude as for ammonium perchlorate. Deflagration occurred with the presence of a molten surface layer and the pulsing phenomenon described above was very pronounced. The results are included in Table VIII.

TABLE VIII

DEFLAGRATION RATES IN FUEL GAS STREAMS

Oxidizer	Fuel Gas	Flow Rate (cm/sec)	Deflagration Rate k^a (cm^2sec^{-1})
AP	CH_4	15.5	0.040
AP	C_3H_8	15.5	0.082
HP	CH_4	15.5	0.065
HP	C_3H_8	15.5	0.040
HDP	CH_4	15.5	0.071
HDP	C_3H_8	15.5	0.112
HDP	C_3H_8	15.5	0.083
HDP	C_3H_8	15.5	0.119

[a] k is defined by $D^2 = D_o^2 - kt$

The experiments we have performed with this technique do not represent an intensive exploration of its possibilities. They do show the difficulties involved in obtaining data in this way.

With ammonium perchlorate our main difficulty has been that the spheres have invariably broken up in the course of an experiment. This has made it impossible to follow the deflagration for more than a fraction of its entire course. With hydrazine diperchlorate the principal difficulty is associated with the nature of the deflagration process. The pulsing phenomenon has resulted in rather erratic data. For hydrazine perchlorate too, the pulsing phenomenon is a complicating feature.

The results of Table VIII indicate that deflagration by this technique proceeds more rapidly in propane than in methane, but in view of the paucity of the data we do not feel this warrants discussion.

C. Discussion

The combustion process is defined by the experimental observations as consisting of three regimes: a high-pressure regime, above approximately 100 atm; a low-pressure regime, below approximately 20 atm; and a region of transition.

The process occurring at high pressure begins to diminish in importance below about 100 atm. This is clearly shown by the fact that the flame temperature falls below theoretical below this point and the deflagration rate decreases at a faster rate below approximately this pressure. Above 100 atm it is considered that "normal" deflagration takes place. By this is meant, a gaseous reaction zone, in which exothermic chemical reactions occur, is stabilized above the strand. Heat is transmitted from this zone back to the condensed material, causing gasification. Reactants enter the flame and thus continue the cycle.

Below approximately 20 atm, the normal deflagration process is making little or no contribution toward the process of reactant consumption. At this pressure the thermal profile begins to lose the character of a combustion wave (Fig. 12). Moreover, condensed phase chemical reactions

are very evident in the motion pictures of strand burning. A gaseous flame is no longer present, or, if there is intermittent gaseous chemical reaction (following pulsing), it is making a secondary heat-transmission contribution. However, the diffusion of reactive chemical species back to the surface must be a major mode of propagation. This is established by the thermal decomposition studies. The low-pressure "combustion" is a rapid thermal decomposition, which is self-sustaining due to chemical reactions in the liquid phase. These in turn are augmented by the impingement and reaction of species from the gas on the surface.

The quenching experiments and the thermal decomposition studies define the overall nature of the chemistry. Hydrazine diperchlorate liberates perchloric acid; $HClO_4$ and/or its decomposition products attack the HP or HDP yielding NH_4ClO_4 and gaseous products. (See Ref. 20 for a hypothesis of the details of this reaction; also in the same paper the decomposition of HP was studied and ammonium perchlorate found to be a major product.) The ammonium perchlorate is only partially recovered and therefore must itself deflagrate. (Preheating pure NH_4ClO_4 allows deflagration to proceed down to at least one atm (3).)

As pressure rises (from $\sim$ 6 to 25 atm) the bubbles in the liquid become smaller and more numerous. Hence, subsurface chemical reactions occur to a greater extent. Accordingly, a pressure exponent greater than unity is called for.

Here the role of catalysts should be mentioned. The action of catalysts in deflagrations is well known (2,3,), but in general is not well understood. In the self-deflagration studies of NH_4ClO_4 and $N_2H_5ClO_4$, there is no evidence for condensed-phase chemical reactions with or without catalysts added, yet catalysts have a profound effect. In the case of ammonium perchlorate (3), there were indications that catalysts were active in altering reactions in the flame zone, although not nearly enough to account for their total accelerating effect on the deflagration. Since the deflagration of HDP, at least at low and intermediate pressures, is characterized by condensed-phase chemical reactions, it see s reasonable

to assume that the role of catalysts, at least in part, is to accelerate these reactions. This might account for the greater effect catalysts have on HDP than on AP or HP. The principal purpose for investigating catalysts in the present research was more to compare their action on HDP with that on ammonium perchlorate and hydrazine perchlorate than it was to understand the mechanism through which catalysts augment deflagration processes. Thus, the study was limited in scope.

In the intermediate pressure region a smooth transition from rapid self-sustained decomposition to normal deflagration is gradually effected. At about 100 atm, thermodynamic equilibrium is attained in the flame. The basic low-pressure mechanism, which includes chemical reactions in the liquid as an essential feature, may continue to be an important aspect of the process in the transition region. Between approximately 25 and 100 atm the pressure exponent remains greater than unity. This can be due to the fact that, not only is heat transmission from flame to strand increasing, but the flame is rising in temperature. At $\sim$ 100 atm the flame temperature attains constancy, thus causing the pressure exponent to assume a value < 1.

In the high-pressure regime, above 100 atm, gasification may continue to occur by chemical attack as at lower pressures. Since, however, the product gas temperature attains the theoretical at this pressure and the slope of the deflagration rate versus pressure curve decreases at approximately this point, one is led to consider an alternative method of gasification at high pressure. This would be the direct vaporization of HDP, i.e., the species entering the flame are not primary products of HDP decomposition but rather N_2H_4 and $HClO_4$. In favor of such a view might be the fact that NH_4ClO_4 is necessarily an intermediate if condensed-phase decomposition is important, but ammonium perchlorate self-deflagration yields a flame temperature 200 - 250° C below theoretical. The theoretical flame temperature is eventually attained in HDP deflagration, thus suggesting that the process might not go through NH_4ClO_4. This point is noted but not pressed since the HDP flame is $\sim$ 400° C hotter than the NH_4ClO_4.

A direct vaporization mechanism must require a higher activation energy than gasification by chemical reaction. Since the surface temperature of solids (and liquids) increases with increasing pressure, it is not unreasonable to expect a dissociative vaporization process at higher pressures.

V. REFERENCES

1. Adams, G.K., B. H. Newman and A. B. Robins, "Selected Combustion Problems: Fundamentals and Aeronautical Applications," Butterworths, London, 1954, P. 387.

2. Friedman, R., R. G. Nugent, K. E. Rumbel and A. C. Scurlock, "Deflagration of Ammonium Perchlorate," Sixth Symposium (International) on Combustion, Reinhold, New York, 1958, pp. 612-618.

3. Levy, J. B. and R. Friedman, "Further Studies of Pure Ammonium Perchlorate Deflagration," Eighth Symposium (International) on Combustion, Williams and Wilkins Co., Baltimore, Md., 1962, pp. 663-671.

4. Audrieth, L. F. and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, 1951.

5. Dushman, S. and J. M. Lafferty, "Scientific Foundations of Vacuum Technique," Second Edition, John Wiley and Sons, Inc., New York, New York, 1962, p. 14.

6. Schultz, R. D. and A. O. Dekker, J. Phys. Chem., 60, 1095 (1956).

7. Inami, S. H., W. A. Rosser and H. Wise, J. Phys. Chem., 67, 1077 (1963).

8. Estimated from the heats of formation of the ions in solution, the heat of hydration of anhydrous hydrazine perchlorate to the hemihydrate and the heat of solution of the hemihydrate.

9. Private communication, G. B. Rathmann, Minnesota Mining and Mfg. Co.

10. McD. Cummings, G. A. and G. S. Pearson, "Perchloric Acid: A Review of its Thermal Decomposition and Thermochemistry," R.P.E. Tech. Note No. 244, Rocket Propulsion Establishment, Ministry of Aviation, London, Oct. 1963.

11. Scott, D. W., et al, J. Am. Chem. Soc., 71, 2293 (1949).

12. Arden, E. A., J. Powling and W. A. W. Smith, Combustion and Flame, 6, 21 (1962).

13. Baer, A. D., N. W. Ryan and D. L. Salt, "Ignition of Composite Propellants, AFOSR-TN-59-516, University of Utah, March, 1959.

14. Lewis, B. and G. von Elbe, "Combustion, Flames and Explosives of Gases," Second Edition, Academic Press, New York, New York, 1961, pp. 620-628.

15. Atlantic Research Corporation, "Research on Combustion in Solid Rocket Propellants," Final Technical Report, Contact No. DA-36-034-AMC-0091R, July 21, 1964.

16. "Temperature--Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, New York, 1941, p. 1313.

17. L. Andrussow, "Diffusion, Viscosity and Conductivity of Gases," Progress in International Research on Thermodynamic and Transport Properties, Academic Press, New York, 1962, p. 279.

18. W. H. McAdams, "Heat Transmission," McGraw Hill Book Company, Inc., New York, 1954, Chapter 10.

19. Rosser, W. A., Inami, S. H., and Wise, H., "Thermal Diffusivity of Ammonium Perchlorate,"Stanford Research Institute, Menlo Park, Calif.

20. Grelecki, C. J. and Cruice, W., "The Thermal Reactions of Some Advanced Solid Oxidizers," paper presented at Symposium on Advanced Propellant Chemistry, Division of Fuel Chemistry, ACS Meeting, Detroit, Mich., April 4-9, 1965.

21. von Elbe, G., and McHale, E. T., "Gasification by Sublimation, Nucleate Boiling, and Chemical Attack in Oxidizer Deflagration Waves," paper presented at 2nd ICRPG Combustion Conference, El Segundo, Calif., Nov. 1-5, 1965.

22. Barrere, M. and L. Nadaud, "The Combustion of Ammonium Perchlorate Spheres in a Flowing Gaseous Fuel," Tenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1965, pp. 1381-1394.

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13 ABSTRACT

The results of research on the deflagration of the solid-propellant oxidizers, hydrazine perchlorate (HP) and hydrazine diperchlorate (HDP), are reported and discussed. Each compound was found to be unique physically and chemically, in both its low-temperature thermal decomposition and its high-temperature deflagration behavior.

HP and HDP are white solids of crystal densities 1.939 and 2.21 g/cc, and melting points of 141 and 191°C, respectively. The following aspects of the combustion process were studied: The deflagration rate as a function of pressure and the effects of catalysts; the flame temperature and the temperature profile through the combustion wave; quenching, thermal decomposition, and chemical behavior. In addition, vaporization rates of HP were measured.

The deflagration of both oxidizers is a non-luminous process and proceeds with a liquid layer. With HP, reproducible results could only be obtained when small amounts of fuel or catalyst were added. The flame temperature was found by the sodium-line reversal method to check the theoretical calculated temperature (2246°K at 1 atm). Temperature-profile measurements through the deflagration wave indicated no heat release in the condensed phase up to 450°C.

With HDP, reproducible self-deflagration was obtained, but the flame temperature (measured by fine thermocouples) was found to be several hundred degrees below theoretical at low pressures. The experimental and calculated product gas temperatures were found to coincide at approximately 100 atm (1604°K). Temperature profile measurements showed that below about 20 atm the profile no longer displayed the shape of that of a normal combustion wave.

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