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Quarterly Technical Summary Report No. 13
June 1, 1965 to August 31, 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 25, D. C.

from
Kinetics and Combustion Group
Atlantic Research Corporation
Alexandria, Virginia

October 11, 1965

Chief Investigators: J. B. Levy
G. von Elbe
Internal Consultant: R. Friedman
Chemist: E. T. McHale
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RESEARCH ON THE DEFLAGRATION OF HIGH-ENERGY SOLID OXIDIZERS (U)

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RESEARCH ON THE DEFLAGRATION OF HIGH-ENERGY SOLID OXIDIZERS

I. ABSTRACT

The flame temperature of hydrazine diperchlorate has been measured using fine Chromel-Alumel thermocouples. At 28 atm the measured temperature was found to be > 200° C below the calculated product gas temperature. The observed temperature increases with pressure, and at approximately 100 atm the theoretical value is attained. The temperature profile through the preheat zone of the combustion wave has been carefully measured at 18 atm. This is found to agree well with that predicted by theory if some variation of thermal diffusivity with temperature is assumed. The thermal profile at low pressure was found not to exhibit the character of that of a normal deflagration wave. This finding has shed considerable light on the nature of the process. Finally, quenching experiments were performed and these are discussed.

II. INTRODUCTION

In this program we are studying the deflagration of a series of high-energy oxidizers. In earlier work in this laboratory the self-deflagration of ammonium perchlorate has been studied in some detail (1). In the present program we have examined the behavior of hydrazine perchlorate and have recently reported our results and conclusions on the deflagration of this oxidizer (2). The investigation of hydrazine diperchlorate (HDP) has been underway for some time and the following lines of research are being pursued: the self-deflagration of HDP in inert gas at elevated pressures; the effects of catalysts on the deflagration rate; the thermal decomposition of HDP, both pure and catalyzed; the measurement of the flame temperature of deflagrating HDP at various pressures and the measurement of the temperature profile through the combustion wave; quenching of the deflagration.

III. PROGRESS DURING PRESENT PERIOD

During the past quarter we have completed the flame tempera-
ture measurements of HDP at various pressures. The temperature profile
through the preheat zone of the deflagration wave at 18 atm has been
carefully measured. Thermal profiles for the deflagration process at
several other pressures have been obtained and have shed light on the
nature of the low-pressure combustion. Quenching experiments were
performed and the results are discussed below.

A. The Flame Temperature of Hydrazine Diperchlorate

The details of the experimental techniques used in measuring
the temperature of the product gases in HDP deflagration have been dis-
cussed in previous reports (3,4). The method is described here in brief
summary form: Fine Chromel-Alumel thermocouples are imbedded in strands
of HDP and the output of these couples is recorded during deflagration.
The thermocouple beads require a radiation correction which depends on
the amount of surface oxidation of the metal. An average correction is
applied which introduces only a small uncertainty in the final flame
temperature.

Previously, the measured flame temperature at 28 atm has been
reported. During the present period, measurements at 55 and 103 atm have
been completed and these are presented in Table I. The measured and
calculated (5) temperatures are shown in Figure 1 as a function of
pressure. In the neighborhood of 100 atm, thermodynamic equilibrium is
attained in the product gases. The temperature then falls rapidly
with pressure until approximately 25 atm. Below this point, the flame
temperature does not lend itself to measurement because of the nature
of the deflagration process. This point is discussed in the following
section.

B. Temperature Profiles Through HDP Deflagration Waves

The thermocouple-output records for deflagrations at 10, 15,
and 21 atm are shown in Figure 2. The profiles do not resemble those
ordinarily obtained in deflagrations of solids, but gradually take on

TABLE I

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

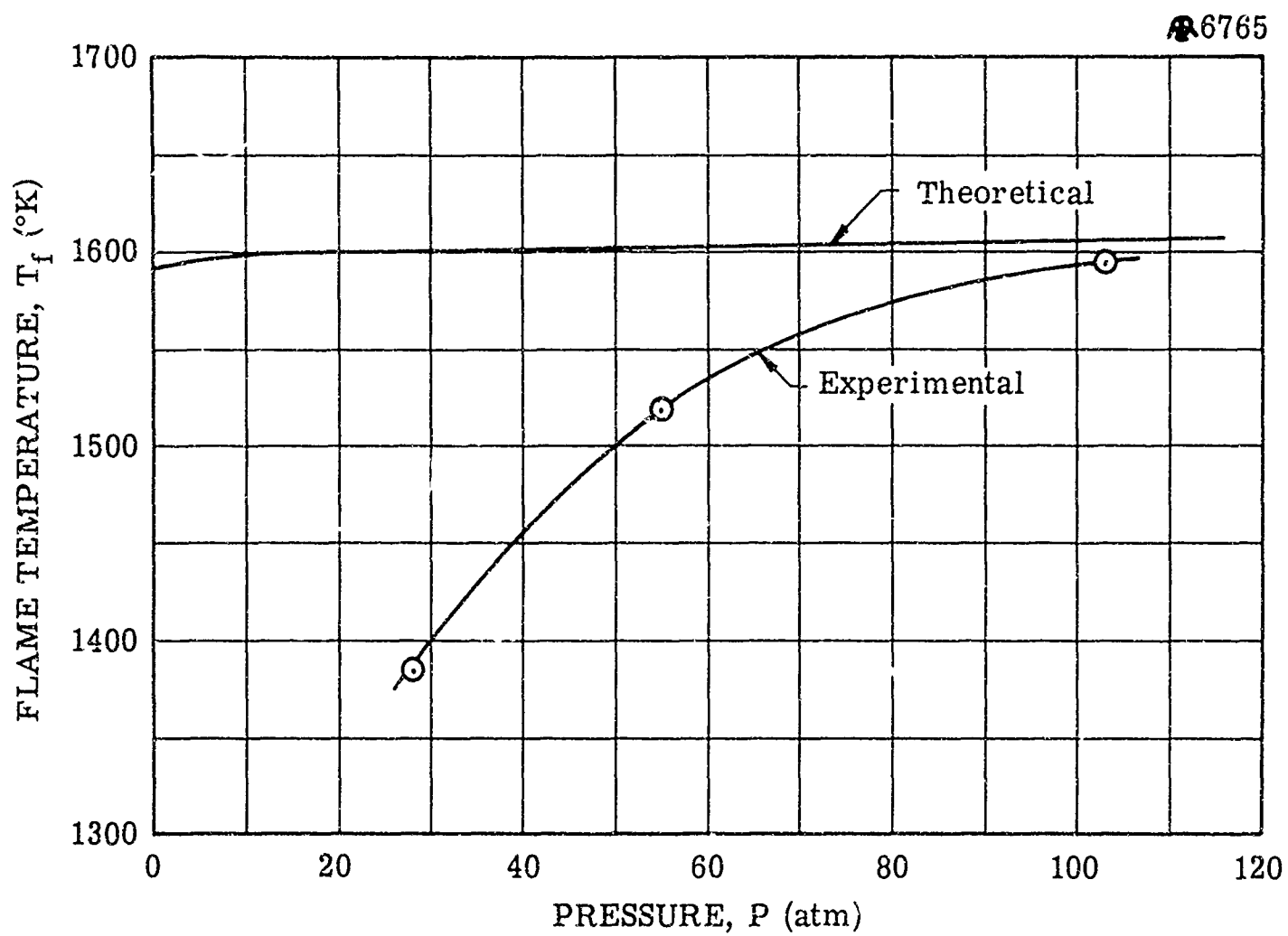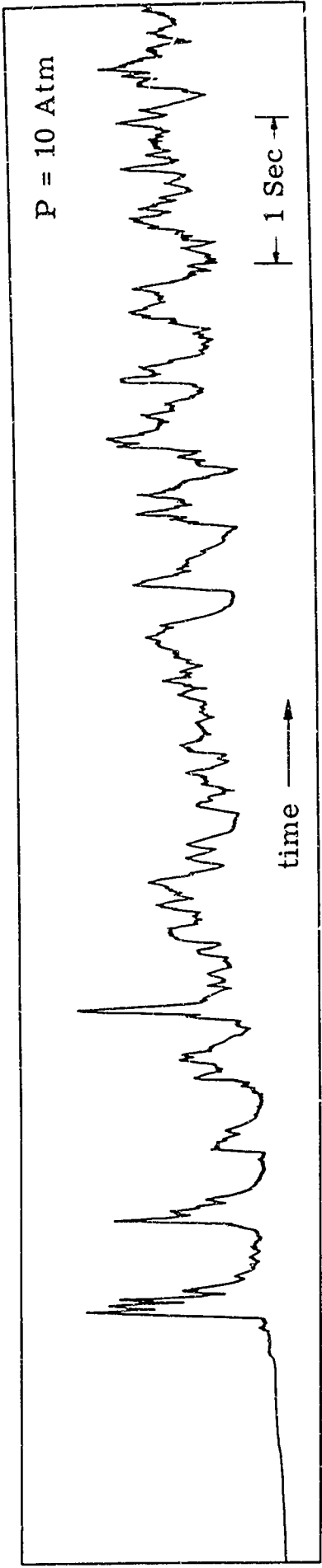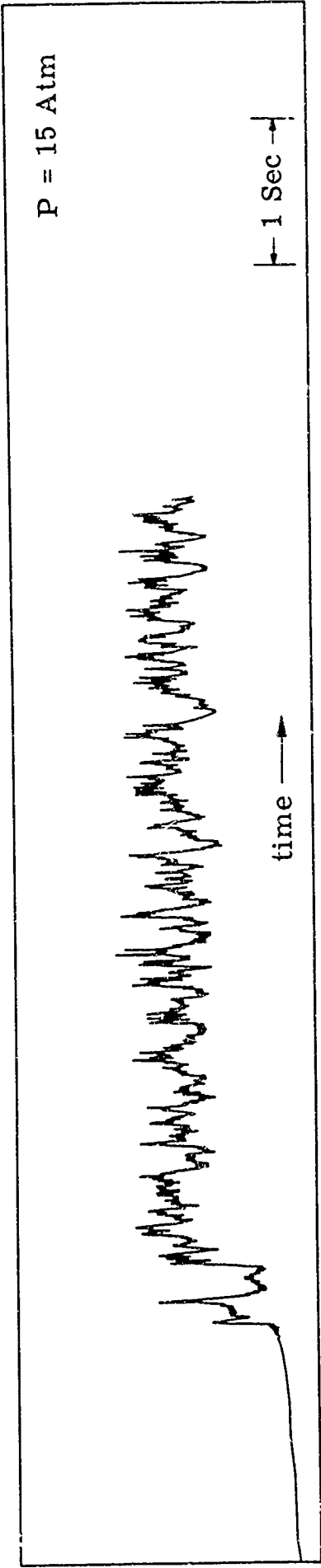| Pressure....................	28 atm	55 atm	103 atm
T observed ($^\circ$K).............	1355	1490	1550
	1355	1465	1545
	1325	1475	
	1370	1510	
	1310	1455	
	1365	1465	
	1365		
	1325		
Average.....................	1345 ± 20	1475 ± 15	1550 ± 5
Radiation correction ($^\circ$K)....	40 ± 15	45 ± 20	45 ± 20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

Figure 1. Flame Temperatures of HDP as a Function of Pressure.

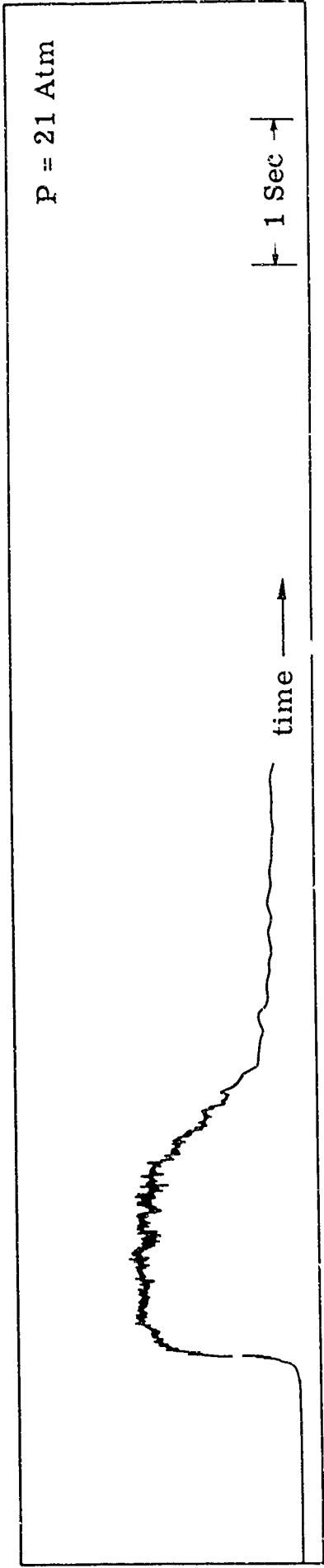6767

Figure 2. Tracings of Thermocouple - Output Records for HDP Deflagrations at Low Pressure.

the shape of a normal flame profile as the pressure increases. Below approximately 20 atm there is no stable flame above the surface of the strand. The erratic temperature fluctuations noted at the lower pressures are due to the "pulsing" phenomena, noted previously (5). By pulsing is meant, 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. Thus, the thermocouple sees random pockets of hot gas. The temperature at which pulsing sets in was not too reproducible, sometimes occurring at or near the melting point, but other times in the neighborhood of 140°C (the melting point of hydrazine perchlorate is 141°C, although this may be fortuitous; the melting point of HDP is 190°C). The low-pressure "combustion" must be regarded as a rapid thermal decomposition, which is self-sustaining due to chemical reactions in the liquid.

In Figure 3a 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 3b. The heat-balance equation which describes the temperature through a combustion wave is

$$\lambda \frac{d^2T}{dx^2} - C_p \, \rho \, r \, \frac{dT}{dx} + Q(x) = 0 \qquad (1)$$

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
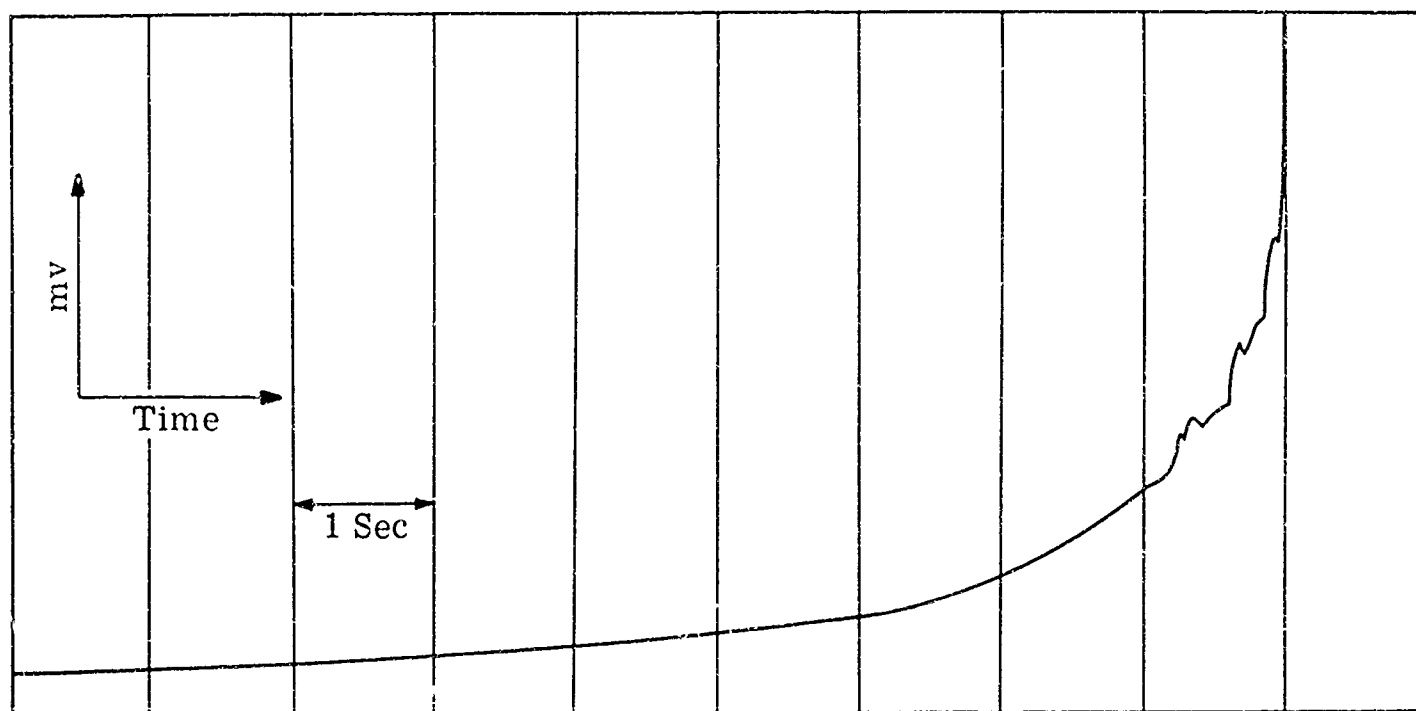
TEMPERATURE (°C)

AR 6764

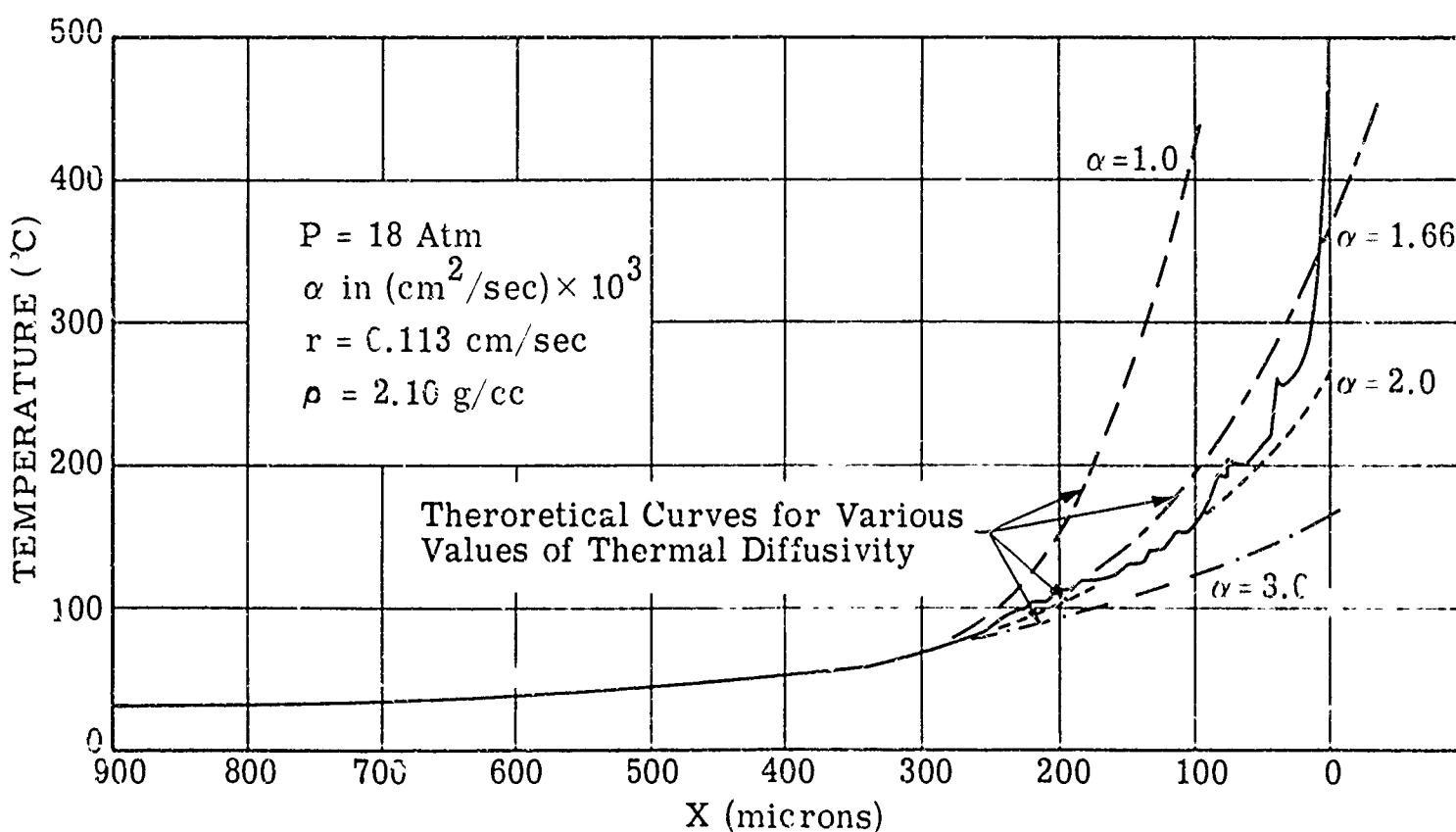Figure 3a. Tracing of Thermocouple - Output Record Through Preheat Zone in HDP Deflagration.

Figure 3b. Temperature Profile Through HDP Deflagration Wave Obtained from above Record.

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 3b, 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 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 (6). A change of the same magnitude for HDP is indicated by the data in Figure 3. 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 2) to fail at lower pressures.

C.   Quenching

In the 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 previous data on deflagration rate as a function of pressure (4) are independent of tube diameter.

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5. Atlantic Research Corporation, "Research on the Deflagration of High Energy Oxidizers," ARPA Order No. 332-63, AF 49(638)-1169. Quarterly Technical Summary Report No. 10, Jan. 19, 1965.

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