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(Unclassified Title)

INVESTIGATION OF THE THERMODYNAMIC
PROPERTIES OF PROPELLANT INGREDIENTS
AND THE
BURNING MECHANISMS OF PROPELLANTS

QUARTERLY PROGRESS REPORT AFRPL-TR-67-263

(1 July 1967 to 30 September 1967)

October 1967

AIR FORCE ROCKET PROPULSION LABORATORY

RESEARCH AND TECHNOLOGY DIVISION

EDWARDS AIR FORCE BASE, CALIFORNIA

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Report Nr. T-0025-3Q-67

QUARTERLY PROGRESS REPORT (U)

(1 July 1967 to 30 September 1967)

October 1967

AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
EDWARDS, CALIFORNIA 93523
CONTRACT NR. FO4611-67-C-0025

SCIENTIFIC PROJECTS LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN 48640

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract Nr. F04611-67-C-0025. The contract was initiated under Air Force Program Nr. 750 G, AFSC Project Nr. 3148, "Investigation of the Thermodynamic Properties of Propellant Ingredients and the Burning Mechanisms of Propellants." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This is the third quarterly report, covering the work performed during 1 July 1967 through 30 September 1967. The Dow Report Number is T-0025-3Q-67.

This work was performed by R. W. Anderson, R. V. Petrella, G. C. Sinke, A. C. Swanson, and L. C. Walker under the technical supervision of Dr. D. R. Stull and Dr. D. A. Rausch, and management supervision of Dr. R. P. Ruh.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

(U)   The heat of formation of carbon tetrafluoride was derived as -223.2 ± 0.6 kcal/mole from measurements of the heat of explosion of mixtures of cyanogen and nitrogen trifluoride. This value, a "key" datum in calorimetry, is in good agreement with recent work from other laboratories.

(U)   Measurements of the heat of explosion of mixtures of hydrogen and trifluoromethoxydifluoroamine were completed. The heat of formation of CF_3ONF_2 was calculated from the data as -189.1 ± 0.8 kcal/mole based on NBS Technical Note 270-1 value for HF (aq).   This result implies a relatively strong bond energy $E(N-O) = 53$ kcal/mole, contrary to some evidence indicating $E(N-O) = 35$ kcal/mole.

(C)   Errors were found in mathematical expressions used for the computerized calculations for experiments previously reported on Beane (BeH$_2$) and ATBH (alane-terminated beryllium hydride polymer). The data were recomputed and now show a higher precision. The heats of formation were slightly revised as follows: Beane, from -5.3 to -5.0 kcal/mole; ATBH, from -33.7 to -35.7 to -35.7 kcal/100 grams.

(C)   Work on DAHTP, Florox, and NF_4BF_4 is in progress.

(U)   The preparation of pure, solvent-free TVOPA has been completed and it has been determined to contain only negligible benzene residue.

(U)   The photochemical process previously used to prepare CF_3NF_2 has been replaced by a process involving low temperature fluorination of KSCN. This process reduces side products and simplifies purification.

(U)   The flash pyrolysis of boron has been studied in the presence of oxygen, fluorine and two prototype monomers. The studies are aimed at minimizing the formation of OH and H_2O and thereby, hopefully, that of HOBO in an air augmented system. Flame temperatures of the various combustion systems are discussed as well as the change of OH concentration.

(U)   The concentration of OH and H_2O are decreased by the addition of elemental fluorine as well as the two prototype monomers CH_2F_2 and CHF_3.

(U)   Recommendations are made to continue the studies of fluorine additives as OH scavengers to decrease the amount of HOBO formed and thereby increase the combustion efficiency of a boron-fueled air augmented system.

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SECTION I

(U)   THERMOCHEMISTRY

A.   HEAT OF FORMATION OF CARBON TETRAFLUORIDE   (U)

1.   Introduction   (U)

(U)   The heat of formation of carbon tetrafluoride is a "key" datum in calorimetry. Carbon tetrachloride appears as a product in fluorine or NF_3 combustion calorimetry of compounds containing carbon. It also appears as a product in oxygen combustion calorimetry of compounds containing carbon and a large percentage of fluorine. In order to reduce calorimetric results to accurate heats of formation, the heat of formation of CF_4 must be well defined.

(U)   The first attempt at measuring the heat of formation of CF_4 was that of von Wartenberg and Schuette (1) in 1933 by direct combination of the elements. Their result is now recognized as much too low. Twenty years later, von Wartenberg (2) published a much higher value based on the reaction of CF_4 and alkali metal to form carbon and alkali fluoride. Kirkbride and Davidson (3) used a similar technique, and some years later Vorobev and Skuratov (4) repeated the work. The results were in agreement to within a few kilocalories but depended on the heat of formation of fluoride ion. Several other investigations were made which used indirect means, including the heat of hydrogenation and decomposition of C_2F_4 (5,6), the heat of combustion of methane in fluorine (7), and the heat of combustion of perfluorocarbons in oxygen (8,9,10,11). None of these was completely independent of the heats of formation of gaseous and/or aqueous hydrogen fluoride quantities not yet well defined.

(U)   Three recent investigations give well defined results. Domalski and Armstrong (12) measured the heat of combustion in fluorine of graphite mixed with Teflon. After correcting for the Teflon, they derived $\Delta Hf^o_{298}(CF_4,g) = -222.87$ kcal/mole. Gre Greenberg and Hubbard (13) measured the heat of combustion in fluorine of pure graphite. After correcting for a small amount of C_2F_6 formed, they derived $\Delta Hf^o_{298}(CF_4,g) = -223.05$ kcal/mole. Concurrently with these direct measurements, we determined the heat of reaction of cyanogen and nitrogen trifluoride with the results described below. In the course of several years of work on the calorimetry of rocket fuels and oxidizers, we have found NF_3 to be a useful fluorinating agent. Recent work in this laboratory has defined the heat of formation of NF_3 as -31.6 ± 0.2 kcal/mole (14,15). The heat of formation of cyanogen was carefully measured by Knowlton and Prosen (16) at the National Bureau of Standards. When preliminary work showed that a mixture of NF_3 and cyanogen exploded when sparked, a full scale measurement was undertaken.

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2. Materials (U)

(U) Both cyanogen and nitrogen trifluoride were purchased from Air Products and Chemicals, Inc. The cyanogen was found to contain about 1% CO_2 as an impurity. This was removed by low temperature distillation through a 3/8" I.D. copper column packed with magnesium beads. The distillation was carried out using a thermocouple detector and recorder usually used for chromatography. Approximately 0.5 g center cuts were trapped out from the helium carrier gas stream. Mass and infrared analysis of the purified material indicated no detectable impurities.

(U) Research grade NF_3 was analyzed by mass and infrared spectroscopy, both of which indicated 0.15% CF_4 as the only impurity. Since the CF_4 could not be further oxidized, it was not necessary to remove it from the NF_3.

3. Nature of the Reaction (U)

(U) Cyanogen and nitrogen trifluoride were found to react in the gas phase when the mixture was sparked according to the equation shown:

$$1/2 \; C_2N_2(g) + 4/3 \; NF_3(g) \longrightarrow CF_4(g) + 7/6 \; N_2(g)$$
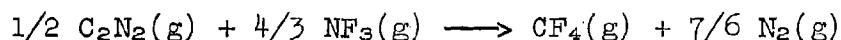
Ignition was accomplished by discharging a standardized capacitor across a 0.5 cm length of nickel fuse wire. An audible "click" could be heard when the reaction took place. The reaction was run with a 3 mole percent excess of nitrogen trifluoride, all of which was dissociated to fluorine and nitrogen during the explosion. Gas samples taken at the conclusion of each experiment were placed in contact with mercury to remove fluorine, and analyzed by mass and infrared spectroscopy. Tetrafluoromethane and nitrogen were the only gaseous products found.

4. Equipment (U)

(U) A Dickinson-type 25°C isothermal shield calorimeter was used for this project. The combustion bomb was constructed of "A" nickel having a volume of 0.3522 l. For vacuum work, O-ring seal needle valves were employed. The energy equivalent of the system was measured by combustion of benzoic acid (National Bureau of Standards sample 391) in oxygen under the prescribed conditions. Eight determinations gave a value of E(calor) = -3200.7 cal/deg with a standard deviation of the mean equal to ± 1.7 cal/deg (1 cal = 4.1840 absolute joules). The following expression was employed to calculate reaction heats from temperature measurements.

$$Qv = E(calor)(t_i - t_f + \Delta t_{cor}) + E^i \; (contents)(t_i - t_n)$$
$$+ E^f \; (contents)(t_n - t_f + \Delta t_{cor})$$

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Temperature measurements were made in terms of the resistance change of a calibrated thermistor - Wheatstone bridge. The corrected temperature changes were calculated by computer using standard procedures.

5. Procedure   (U)

(U) After the benzoic acid calibration experiments, the nickel bomb was passivated by carrying out several preliminary C_2N_2-NF_3 reactions. Between reactions, the bomb was kept under vacuum and opened only in a nitrogen dry box. After four explosion reactions, the internal surfaces of the bomb were noticeably glazed with NiF_2.

(U) A determination involved first fitting a weighed nickel fuse between the electrodes of the bomb while in the drybox. The bomb was then evacuated for several hours to less than one micron pressure. Cyanogen, contained in a 10 ml stainless steel cylinder, was metered into the bomb to a pressure of about 350 mm. The bomb was closed and the cyanogen in the manifold condensed back into the small cylinder. The mass of cyanogen contained in the bomb was determined by weighing the cylinder before and after the loading. Nitrogen trifluoride was admitted to the bomb to a total pressure of 1335 mm using the same procedure.

(U) After the heat measurement, the bomb was again attached to the vacuum line for gas sampling and evacuation. The bomb was then opened in the dry box and unburned pieces of nickel fuse wire recovered. These were cleaned and weighed to determine the net amount burned to NiF_2. Data for this correction were available (17).

6. Results   (U)

(U) Table I lists the results of ten determinations. Qv is the calorimetrically determined heat derived from the temperature change. Column three is the NF_3 dissociation correction based upon the amount of excess NF_3 over stoichiometry. Columns four and five are corrections for nickel fuse wire consumed as NiF_2 and the electrical energy necessary for fusion, respectively. These have been discussed earlier. Column six lists the standard state internal energy change per gram of cyanogen.

(U) The average $\Delta E_r^\circ/M$ from Table I and a molecular weight of 52.0357 for cyanogen yields for the reaction at 298.15°K :

$$1/2\ C_2N_2(g)\ +\ 4/3\ NF_3(g)\ \longrightarrow\ CF_4(g)\ +\ 7/6\ N_2(g)$$
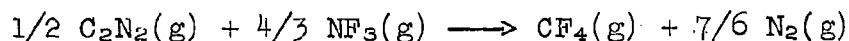
$$\Delta E_r^\circ = -218.33 \pm 0.20\ \text{kcal}$$
$$\Delta n(gas) = +1/3\ \text{mole}$$
$$\Delta nRT = +0.20\ \text{kcal}$$
$$\Delta H_r^\circ = -218.13 \pm 0.20\ \text{kcal}$$

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Table I

(U) Heat of Reaction of Cyanogen and Nitrogen Trifluoride

| Run No. | C_2N_2, g | Qv, cal | Corr. in cal | | | $\Delta Er°/M$ cal/g |
			NF_3	Fuse	Ign.	
3	0.3496	-2,919.0	-17.0	3.7	0.4	-8,386.4
6	0.3496	-2,925.8	-10.8	4.0	0.4	-8,387.3
8	0.3515	-2,947.1	- 8.0	4.3	0.6	-8,393.2
9	0.3495	-2,992.6	-16.6	2.9	0.6	-8,399.7
11	0.3488	-2,929.8	-12.7	3.5	0.4	-8,399.6
12	0.3518	-2,954.9	-11.7	3.4	0.6	-8,399.4
13	0.3519	-2,946.7	-10.0	4.4	0.6	-8,373.7
14	0.3510	-2,947.6	-10.9	4.2	0.4	-8,397.7
15	0.3518	-2,942.8	-15.8	3.8	0.7	-8,372.1
16	0.3515	-2,955.2	-11.3	4.1	0.7	-8,407.4

Avg. = -8,391.6 cal/g

Standard deviation = 3.7 cal/g

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Taking $\Delta Hf^{\circ}_{298.15}(C_2N_2,g) = +73.85 \pm 0.4$ kcal/mole

and $\Delta Hf^{\circ}_{298.15}(NF_3,g) = -31.6 \pm 0.15$ kcal/mole.

we calculate $\Delta Hf^{\circ}_{298.15}(CF_4,g) = -223.23 \pm 0.6$ kcal/mole.

This result is in excellent agreement with the previously quoted values from fluorine combustion of graphite. A weighted average of -223.0 kcal/mole is recommended for future use.

B. HEAT OF FORMATION OF TRIFLUOROMETHOXYDIFLUOROAMINE (U)

1. Introduction (U)

(U) Trifluoromethoxydifluoroamine (CF_3ONF_2) was first prepared and characterized by G. H. Cady and L. C. Duncan several years ago. It was first described in the open literature by Hale and Williamson (18). In order to define the contribution of the $-ONF_2$ group to the heat of formation of a molecule, the heat of formation of this compound was measured.

2. Materials (U)

(U) The sample was prepared at the Dow Scientific Projects Laboratory. The methods of synthesis and purification have been preivously described in the first quarterly report of this year. A batch of five grams was provided.

(C) Molecular weight measurements were carried out by measuring the gas density at 22°C. These measurements, when corrected for gaseous non-ideality using estimated critical constant and the Berthelot equation of state, yielded 137.0 ± 0.1 g/mole for the molecular weight. Theory is 137.01 g/mole. The analytical results described later also indicate the sample was of high purity.

(U) Ultra-high purity hydrogen from Air Products and Chemicals, Inc., was used without further treatment. Mass and infrared spectral analysis detected no impurities.

3. Equipment (U)

(U) An Argonne National Laboratory type of rotating bomb calorimeter was used for this project. The platinum-lined combustion bomb had been fitted with an external tank so that water could be forced into the bomb after an explosion reaction. This apparatus has been described in an earlier report (19). O-ring sealed valves were employed for vacuum work.

(U) The energy equivalent of the system was measured by combustion of benzoic acid (NBS sample 391) in oxygen under the prescribed conditions. Eleven determinations gave a value of E (cal) = 3352.1 cal/deg with a standard deviation of the mean equal to 2.4 cal/deg (1 cal = 4.1840 absolute joules). This value was adjusted to 3402.0 cal/deg for the conditions of the

CF_3ONF_2 experiments. Temperature measurements were made in terms of the resistance change of a calibrated thermistor - Wheatstone bridge. The corrected temperature changes were calculated by standard procedures.

4. Nature of the Reaction (U)

(U) Exploratory experiments carried out in a platinum-lined reaction bomb indicated that CF_3ONF_2 underwent reduction to CO, HF and N_2 when sparked with a 10-20% excess of H_2. Fifty ml of H_2O was then forced into the bomb and the bomb rotated to produce a homogeneous solution of aqueous HF. The reaction is shown below:

$$CF_3ONF_2(g) + 5/2\ H_2(g) \longrightarrow CO(g) + 1/2\ N_2(g) + 5\ HF\ (1:150\ H_2O)$$
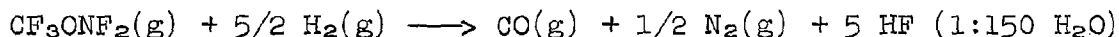
(U) Mass and infrared spectral analysis of the gaseous products showed only CO and N_2. The calorimetric experiments were followed by an analysis for CO by sweeping the bomb gases through a furnace and collecting and weighing the CO_2 formed. A side reaction was indicated by the fact that CO analyses were low by 1 to 2%. Slight carbon deposits were observed around the electrodes, indicating the side reaction to be:

$$CO(g) + H_2(g) \longrightarrow C(s) + H_2O(l)$$

Corrections for this reaction could be applied, based upon the CO_2 recovery in each experiment.

(U) Reactions at 1-2% excess H_2 were carried out for analytical purposes to establish the purity of the CF_3ONF_2. These reactions yielded CO, N_2, and HF as in the former case; however, a few tenths of a percent of HNF_2 was observed by mass spectral analysis. No spots of carbon were observed in these determinations and carbon recoveries were complete within the limits of error. The HF solution was titrated with base to determine the total equivalents of acid; however, this determination was consistently short both in the purity experiments and in the calorimetric runs. Table II gives the analytical data.

Table II

(U) Analytical Data for Trifluoromethoxydifluoroamine

	Experiment No. 1	Experiment No. 2
Sample mass, g	0.5246	0.2031
CO_2 recovered, mg	169.24	65.22
Theory, %	100.4	100.0
HF recovered, meq	18.6	
Theory, %	97.2	

5. Procedure (U)

(U) The bomb was first dried and evacuated to one micron pressure on a vacuum manifold. A one-half gram portion of CF_3ONF_2 was then metered into the bomb to 200 mm pressure from a weighed steel U-tube fitted with miniature Hoke valves. The bomb was closed off after the charging and the amount of sample in the system condensed to a total pressure of 800 mm with hydrogen. To complete the loading operation, the external annular tank on the bomb was loaded with 50 ml of water and charged to 60 psig with argon.

(U) The loaded bomb was placed in the calorimeter and after the initial drift rate was established, the gaseous mixture was ignited. A few seconds later, the tank valve was tripped and water was forced into the bomb. After a few more seconds, bomb rotation was started to ensure a homogeneous final aqueous solution. Final drift rate measurements completed the energy determination.

(U) The bomb was removed from the calorimeter and the gases discharged through an analytical train to determine carbon as CO_2. The bomb was then opened and carefully washed out with distilled water. The solution was analyzed for HF by titration with standard base.

6. Results (U)

(U) Table III lists the results of eight experiments. Q_v is the calorimetrically determined heat change in calories. The carbon correction arises from a small amount of $CO(g)$ being reduced to carbon during the explosion. This reaction is exothermic and amounts to 40.718 kcal/g atom of carbon. Column five is a correction based upon the energy released when a standardized capacitor is discharged during ignition. $\Delta E_r^\circ/M$ is the internal energy change in calories per gram of CF_3ONF_2.

(U) The average $\Delta E_r^\circ/M$ from Table III and the molecular weight of 137.009 for CF_3ONF_2 yield for the reaction at 298.15°K:

$$CF_3ONF_2(g) + 5/2\ H_2(g) \longrightarrow CO(g) + 1/2\ N_2(g) + 5\ HF\ (1:150\ H_2O)$$
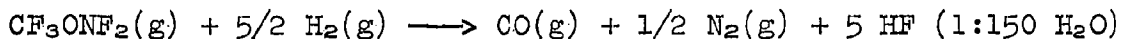
$$\Delta E_r^\circ = -217.85 \pm 0.80\ \text{kcal/mole}$$

$$\Delta n(gas) = -2\ \text{moles}$$

$$\Delta nRT = -1.18\ \text{kcal/mole}$$

$$\Delta H_r^\circ = -219.03 \pm 0.80\ \text{kcal/mole}$$

From Reference 20:

$$\Delta Hf^\circ_{298}\ (HF \cdot 150\ H_2O) = -76.35\ \text{kcal/mole}$$

$$\Delta Hf^\circ_{298}\ (CO, g) = -26.42\ \text{kcal/mole}$$

Table III

(U) Heat of Reaction of Gaseous Hydrogen and Trifluoromethoxydifluoroamine

Run No.	Sample Mass, grams	Q_v, calories	Corrections, calories		$-\Delta E^\circ_r/M$ cal/g
			Carbon	Ign.	
1	0.5886	942.4	(2.3)*	0.3	1,596.2
2	0.5244	838.2	(2.3)*	0.3	1,593.4
5	1.0492	1,683.2	3.7	0.4	1,600.4
6	0.5254	835.9	1.2	0.2	1,588.3
7	0.5216	833.7	3.1	0.2	1,592.0
8	0.5250	829.0	2.8	0.3	1,573.1
9	0.5263	837.9	2.2	0.3	1,586.4
10	0.5247	836.6	1.6	0.7	1,590.0

Avg. = 1,590.0

Std. dev. = 2.8

* Note: Carbon corrections for Runs 1 and 2 were estimated from Runs 5 to 10.

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From these values we calculate:

$$\Delta Hf^{\circ}_{298}(CF_3ONF_2, \text{ g}) = -189.1 \pm 0.8 \text{ kcal/mole.}$$

The uncertainty is equal to twice the overall standard deviation of the experiments.

7. Bond Energy Comparisons (U)

(U) It is of interest to compare our experimental result with predictions from bond energy terms. We shall use the bond energy terms and heats of atomization adopted in a recent publication from this laboratory (21) and listed in Table IV.

Table IV

(U) Terms for Calculation of Heats of Formation

$$E (C-F) = 117.5 \text{ kcal/mole}$$
$$E (N-F) = 67.1 \text{ kcal/mole}$$
$$E (C-N) = 65.2 \text{ kcal/mole}$$

$$\Delta Hf (C,g) = 171.3 \text{ kcal/mole}$$
$$\Delta Hf (N,g) = 113.0 \text{ kcal/mole}$$
$$\Delta Hf (F,g) = 18.9 \text{ kcal/mole}$$

Resonance energy of CF_3 group is 1.4 kcal per bond less than that of CF_4.

Resonance energy of CF_2 group is 6.4 kcal per bond less than that of CF_4.

In addition, the heat of atomization of oxygen is taken from Reference 20 as 69.55 kcal/mole and bond energies $E (C-O) = 85.5$ and $E (N-O) = 53.0$ kcal/mole are from Reference 22. There is then calculated:

$$-\Delta Hf = \Sigma \text{ (bond energies)} - \Sigma \text{ (heats of atomization)} + K$$

where K is any correction term for resonance, steric effects, or other terms.

$$-\Delta Hf = 625.2 - 438.4 - 4.2$$
$$\Delta Hf^{\circ}_{298}(\text{g}) = -182.6 \text{ kcal/mole}$$

(U) This is slightly less negative than experimentally measured which implies that CF_3ONF_2 is a relatively stable molecule. This is in agreement with the observation of Hale and Williamson (18) that CF_3ONF_2 is stable at 140°C. At higher temperatures, cleavage to CF_4 and FNO occurred. Our result is not in accord with a bond energy $E (N-O) = 35$ kcal, which might be inferred from work of Paulett and Lustig (23) on mass spectrometer appearance potentials from FSO_2ONF_2.

C. REVISED HEATS OF FORMATION OF BEANE AND ATBH (U)

(C) Heats of formation of lithium-doped crystalline BeH_2 and alane-terminated beryllium hydride polymer (ATBH) were given in previous reports. In the course of work since completion of those projects, it was discovered that the mathematical expression for converting the automatic bridge resistance readings to temperature was in error. The data for these two projects were recomputed. The results now show a precision twice as high as originally re-- ported. The derived heats of formation changed slightly as given in Table V. Complete recalculated tables of data will be included in the 1967 Annual Report.

Table V

(U) Revised Heats of Formation of Beane and ATBH

	Originally Reported	Recalculated
BeH_2	-5.3 kcal/mole	-5.0 kcal/mole
ATBH	-33.7 kcal/100 g	-35.7 kcal/100 g

D. WORK IN PROGRESS (U)

(C) Exploratory experiments have shown that one gram of ammonium perchlorate can be completely decomposed if a sample is placed in a platinum crucible as loose grains along with a pellet of benzoic acid which is burned as usual in an oxygen bomb. This technique will be applied to diammonium hydrazinium tetraperchlorate (DAHTP).

(C) A sample of Florox (ClF_3O) has been received from Rocketdyne Corporation. It is planned to attempt reaction with aqueous hydrazine sulfate as a calorimetric study. Calibration of the calorimeter is in progress.

(C) A sample of tetrafluoroammonium fluoroborate (NF_4BF_4) has been ordered from Shell Development Company. It is planned to attempt decomposition in an oxygen bomb in a fashion similar to that described above for ammonium perchlorate.

E. SYNTHESIS (U)

(U) The preparation of pure, solvent-free TVOPA has been completed with the determination of residual benzene in TVOPA using labeled benzene. Previously reported results indicated that the radioactivity remaining was due to a nonvolatile material present in the radioactive benzene sample rather than to benzene itself. An experiment with a new lot of radioactive benzene confirmed this. A sample of TVOPA was treated with labeled benzene, which was subsequently removed. Another sample of TVOPA was then treated similarly, with the benzene removed from the previous sample. Both samples contained only negligible radioactive residue from the

standpoint of making corrections in the thermal data.

(U)   Synthesis and purification of CF_3NF_2 has been renewed. The formation of CF_3NF_2 by a photochemical process was reported previously, i.e.,

$$CF_3I + N_2F_4 \xrightarrow[\text{Corex Filter}]{h\nu} CF_3NF_2$$
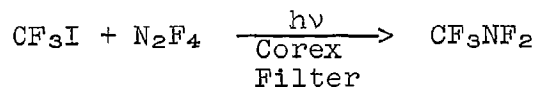
However, this process gave many side products, including SiF_4 and nitrogen oxides, which were very difficult to separate from the desired material.   A better method of preparation involving low temperature direct fluorination of KSCN has been used recently, viz. (24).

$$KSCN + 6\ F_2 \xrightarrow[-80^\circ C.]{KF} CF_3NF_2 + SF_6 + KF$$
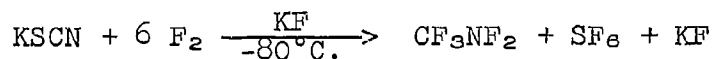
The yield is quantitative and the gaseous products consist almost entirely of CF_3NF_2 and SF_6. By carefully codistilling the reaction mixture twice, 0.88 g of relatively pure CF_3NF_2 has been obtained. This material has been delivered to the Thermal Research Laboratory for use in preliminary measurements.

(U)   Additional material has been prepared, but it became contaminated with nitrogen oxides. Apparently CF_3NF_2 reacted with a contaminant in either the vacuum system or the codistillation apparatus to produce nitrogen oxides.

(U)   In the future, an addition 6 g of pure CF_3NF_2 will be prepared.

SECTION II

(U) COMBUSTION KINETICS

A. INTRODUCTION (U)

(C) In an air augmented combustion system, the prime purpose of the solid propellant combustion is to supply boron fuel to the air-supported combustion process. The combustion efficiency of boron or a boron-containing fuel seems to be limited by the modes and rate of formation of metastable species, especially HOBO.

(U) One possible way to increase combustion efficiency is to modify the composition of the solid propellant to effect a reduction of the concentration of the chemical species which produce HOBO. It has been shown that HOBO is formed from both BO_2 (25) and B_2O_3 (26,27) reacting with water formed during combustion of the oxidizer, NH_4ClO_4 (AP), and the hydrogen-rich binder.

(U) Two possible ways to reduce the formation of water and its intermediate OH are to either decrease the amount of hydrogen-containing components in the propellant formulation or to modify the composition of the components to minimize the formation of water and OH. A change in the composition of a solid propellant results directly in a change in the flame temperature and in the distribution of combustion products (28).

(C) In an air-supported oxygen oxidized system, the temperature for ignition of the boron must be in excess of 2200°K (29). Thus, any combustion system supplying elemental boron to the air-supported combustion process must have a flame temperature in excess of ~2300°K. In addition, it is imperative to determine the flame temperature for any modified system supporting air augmented combustion.

(C) Since the oxidizer, AP, is rich in hydrogen, it is not feasible to decrease the amount of all hydrogen compounds. Instead, one should try and modify the binder in such a way as to minimize the amount of H_2O and OH formed.

(C) It was decided to investigate the effects of a fluorine-containing binder on the formation of H_2O and OH and on the flame temperature of a burning boron-oxygen system. If most of the hydrogen generated by the pyrolysis of the oxidizer and binder was to react with the fluorine, the preferential formation of HF would preclude the formation of OH and H_2O.

(C) The study of the effect of fluorine atoms on the combustion of boron in oxygen was studied in several systems by flash pyrolysis and kinetic spectroscopy.

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B. EXPERIMENTAL (U)

(U) The flash pyrolysis apparatus employed has already been described (30). The elemental analysis of boron used in the present work, "Avco 400", has already been reported (31). The fluorine was ob ined from the Matheson Company and was 98.5% pure. The compounds CH_2F_2 and CHF_3, prepared by Dow, were 99 mole percent pure.

(U) All combustion studies were initiated by a 2000 joule flash. Initial analyses were made at a delay time of 100 μsec and analyzed for as long as 2.5 milliseconds after initiation. The data were recorded by photographing the absorption spectrum of each reaction in the spectral range 2000-6000 Å, using Kodak 103-0 and 103-F spectroscopic plates.

(U) The compositions of the systems studied were:

$$
\begin{array}{lll}
(\text{i}) & \sim 45 \text{ mg boron}/30 \text{ mm } O_2 \\
(\text{ii}) & \sim 45 \text{ mg boron}/20 \text{ mm } O_2/18 \text{ mm } H_2O \\
(\text{iii}) & \sim 45 \text{ mg boron}/10 \text{ mm } O_2/10 \text{ mm } F_2 \\
(\text{iv}) & \sim 45 \text{ mg boron}/15 \text{ mm } O_2/30 \text{ mm } F_2 \\
(\text{v}) & \sim 45 \text{ mg boron}/25 \text{ mm } O_2/10 \text{ mm } CH_2F_2 \\
(\text{vi}) & \sim 45 \text{ mg boron}/25 \text{ mm } O_2/10 \text{ mm } CHF_3 \\
\end{array}
$$

(U) The first two systems, (i) (30) and (ii) (32), were studied to give base line values for the effect of water on the combustion of boron in oxygen.

(C) Systems (iii) and (iv) were studied to show the effect of fluorine atoms on the combustion of boron in oxygen, and, in particular, to determine the extent of reduction of the OH radical concentration. Hydrogen was always present in our system as a result of the 0.8% hydrogen in the boron itself plus that due to the Apiezon stopcock grease needed to bond the boron to the graphite plates used in our pyrolytic technique. Systems (v) and (vi) were studied to determine the effect of introducing fluorine atoms at two different H/F ratios in the prototype monomers into the solid propellant system. Primary consideration was given to the distribution of combustion products and to the flame temperature for each of the above systems, since the flame temperature of the solid propellant combustion process greatly influences the amount of boron supplied to the incoming air, as well as the physical state of the boron [M.P. = 2450°C (33)].

(C) The proposed stoichiometry of the reaction between oxygen and CH_2F_2 is:

$$CH_2F_2 + O_2 \longrightarrow CO_2 + 2 \text{ HF} \tag{1}$$
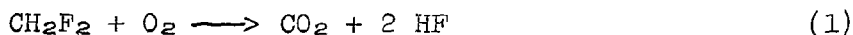
The reaction between O_2 and CHF_3 is proposed to be:

$$CHF_3 + O_2 \longrightarrow CO_2 + HF \text{ 2 F} \tag{2}$$
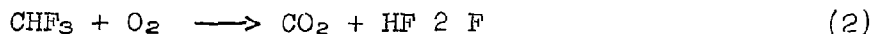
(C) System (v) was studied to determine the effect of a prototype binder, CH_2F_2, which was stoichiometrically balanced to form HF by itself, on the reaction between boron and oxygen. System (vi) is an example of a fluorine-rich system (one which has an F/H ratio >1). The excess fluorine is available to react with the hydrogen from the oxidizer as well as from the plasticizer.

(U) Thermochemical calculations show that if BF_3 and H_2O were found, instead of B_2O_3 and HF at 2500°K, the reaction:

$$2\ BF_3(g) + 3\ H_2O(g) \longrightarrow B_2O_3(g) + 6\ HF(g) \tag{3}$$
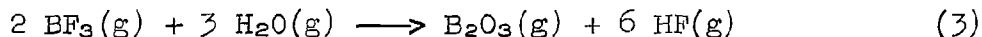
would have a free energy of -33.3 kcal. This negative value for the free energy means the right side of (3) would be favored. The overall effect of the fluorine would be to minimize the formation of H_2O and, hopefully, that of HOBO.

(U) Plate intensities were read with a Jarrell-Ash ratio recording microphotometer. A mercury arc was used to calibrate the spectrograph and the spectroscopic plates.

(U) The flame temperature was inferred from the rotational distribution of the (0, 0) band of the $A^2 \Sigma^+ - X^2 \Pi$ transition of the OH radical (33). The technique is that of Dieke and Crosswhite (34) and involves the distribution of intensity among lines of the rotational fine structures of a band spectrum. A discussion of the merits of the technique can be found in NBS Circular 523 (35).

(U) The experimental observations are discussed below. Analysis and interpretation of these observations are presented later in the Discussion Section.
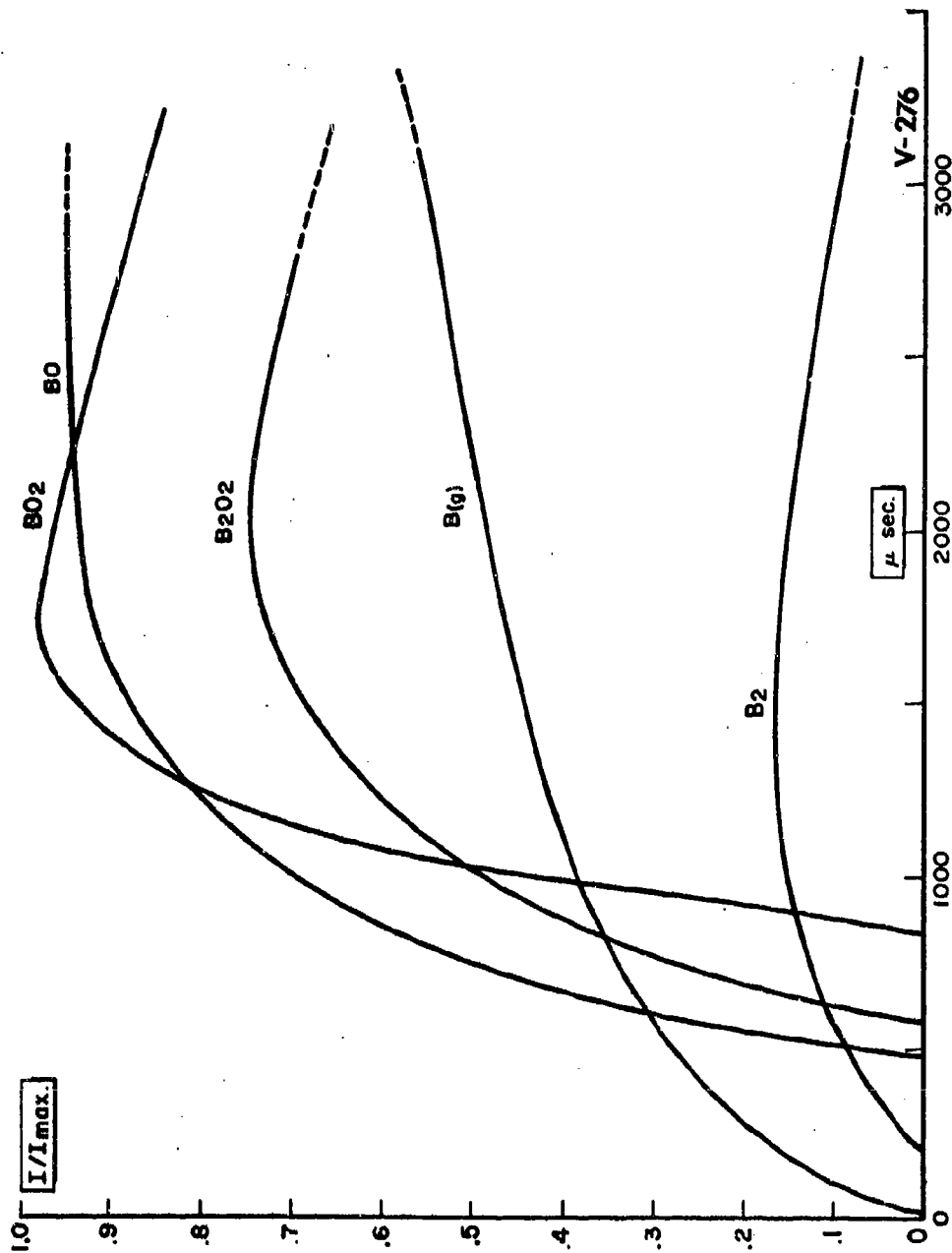
C. EXPERIMENTAL RESULTS (U)

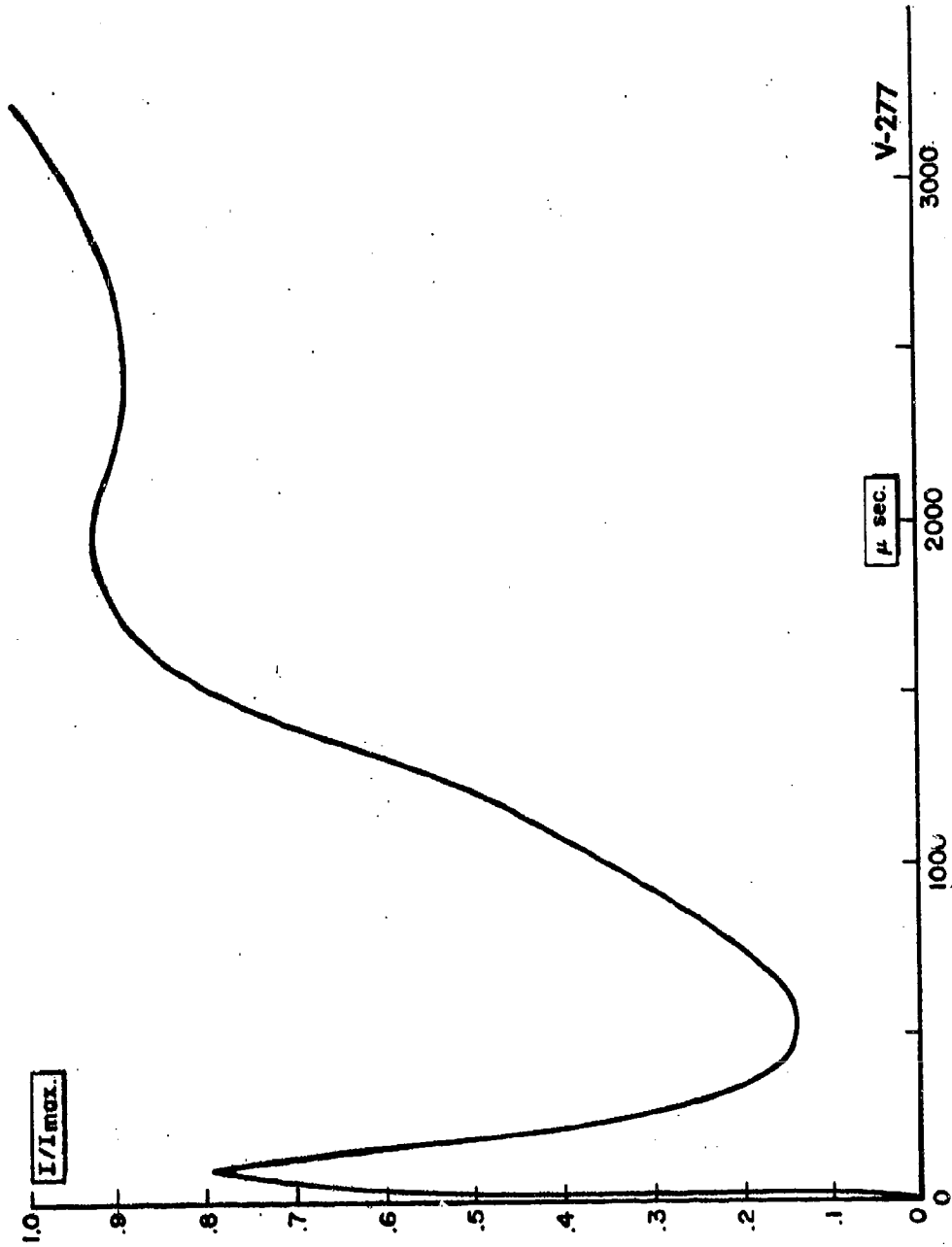### 1. Combustion of Boron in Oxygen and Water (U)

(U) The experimental results and the discussion for the combustion of boron in oxygen and in a mixture of oxygen and water has been previously described (32). However, the calculation of the flame temperatures for these systems had not been carried out at that time.

(U) Figure 1 shows the correlative intensity of boron species observed during the combustion of boron in 30 mm of O_2. The relative concentration of the OH radical observed during the same reaction is seen in Figure 2. The second and more prominent OH maximum seems to correspond in time to the rate of formation of BO_2. The OH intensity is about 30% of that for BO_2 at maximum intensity. The hydrogen for this weak OH spectrum probably came from the stopcock grease "glue" used to bond the boron to the graphite strip as well as from the 0.8% hydrogen in the boron metal itself.

(U) The flame temperature of the boron-oxygen system discussed above is shown in Figure 3. The lines through the

(U) Fig. 1 - Boron Species Observed During the Flash Pyrolysis f Boron in 30 mm Oxygen at 2000 Joules in System (1)

I/Imax.

1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0

0   1000   2000   3000   V-277

μ sec.

(U) Fig. 2 - Hydroxyl Radicals Observed During the Flash Pyrolysis of Boron in 30 mm Oxygen at 2000 Joules in System (1)

experimental points are the uncertainty in the temperature measurement. The maximum in the flame temperature correlates quite well with the first significant appearance of BO_2 at about 1000 µsec after initiation. The steady state flame temperature of about 2350-2400°K is reached at about 2000 µsec after initiation. This corresponds in time to the steady state concentration of BO being attained (compare Figures 1 and 3).

(U) There seems to be no direct correlation between the flame temperature and the OH concentration for the boron-oxygen system other than both approach some equilibrium value at about 2000 µsec (Figures 2 and 3).

(U) The time-intensity curve for the OH radical observed during the combustion of boron in the presence of oxygen and water is shown in Figure 4. The total intensity of the OH in Figure 4 is about 10 times that in Figure 2. The total intensity of BO and BO_2 are reduced to a value below that seen in Figure 1.

(U) The flame temperature for the boron-oxygen-water system is seen in Figure 5. The lack of coincidence of the flame temperature with the OH radical concentration indicates that the process or processes which give rise to the initial large amount of OH are not necessarily those which govern the combustion temperature of boron in an oxygen/water mixture. The profile of the flame temperature which occurs at times greater than 1000 µsec seems to parallel the concentration change of the OH radical during the same time period. This could indicate that the process which governs the rate of formation and disappearance of the OH radical could also control the temperature of the whole combustion process.

(U) It is important to note that the addition of water to a boron-oxygen system reduces the maximum flame temperature by about 300°K. This effect is in the direction indicated by the reaction:

$$H_2O(g) + BO_2(g) \longrightarrow OH + HOBO \qquad \Delta H_{R\ 2500} = +7.5 \text{ kcal} \qquad (4)$$
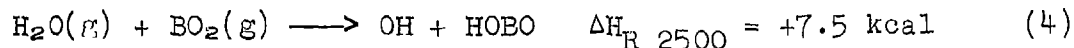
2. Combustion of Boron in Fluorine and Oxygen (U)

(U) Detailed analysis of these combustion systems has not been completed; however, certain gross features were observed. The products at 100 µsec in both Systems (iii) and (iv) were primarily BF and HF. The BF/HF ratio was greater in the fluorine-rich System (iv) than it was in the System (iii).

(U) The OH intensity was reduced considerably by the addition of fluorine, showing the preferential formation of HF over OH. The OH intensity is about 15-20% of that of a boron-oxygen system.

(U) The maximum flame temperature for System (iii) which contained equal amounts of fluorine and oxygen was 2663 ± 37°K, as shown in Figure 6. The flame temperature for a boron/oxygen/flame
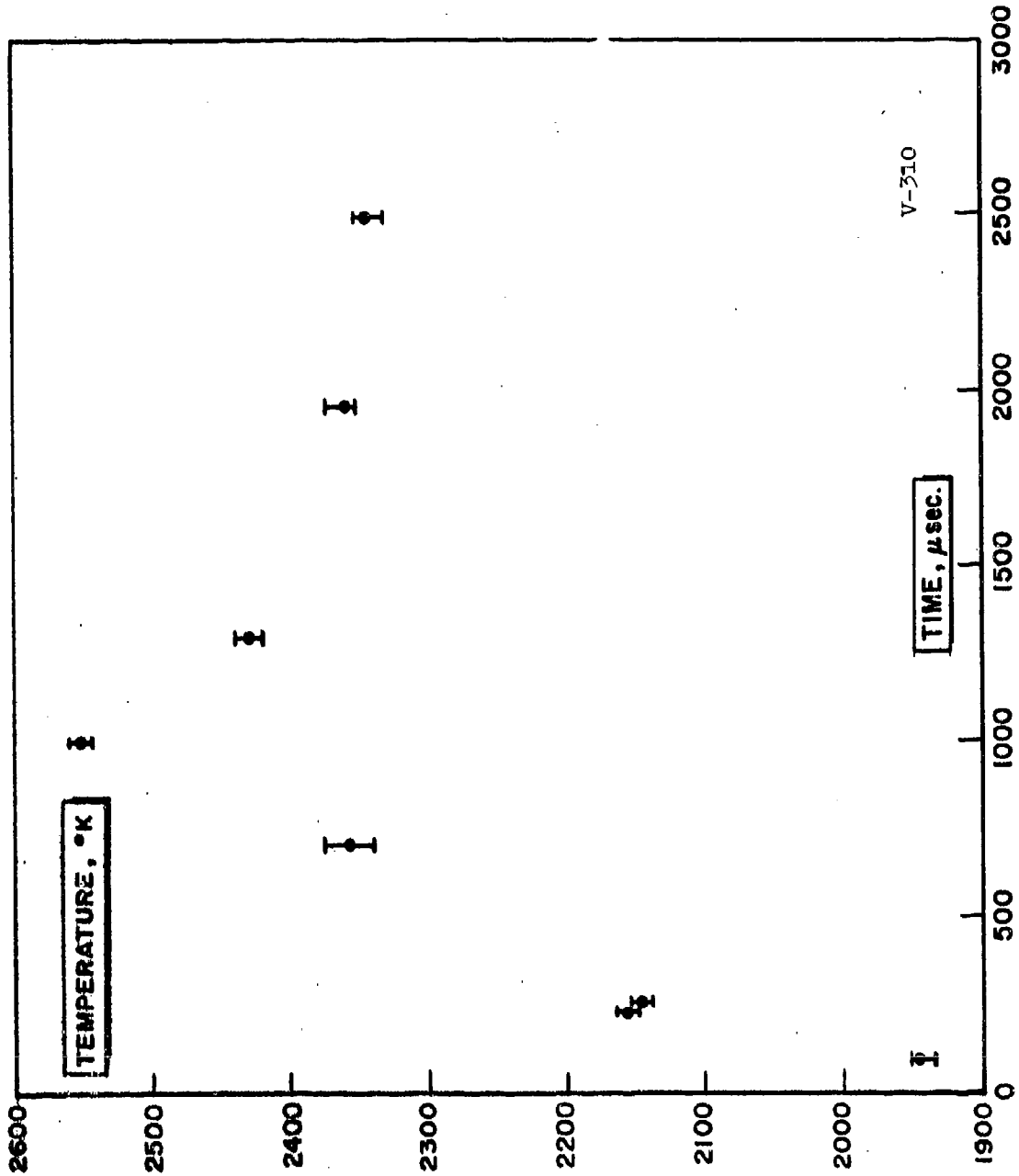
(U) Fig. 3 - Flame Temperature Observed During the Combustion of Elemental Boron in Oxygen in System (1)

AFRPL-TR-67-263
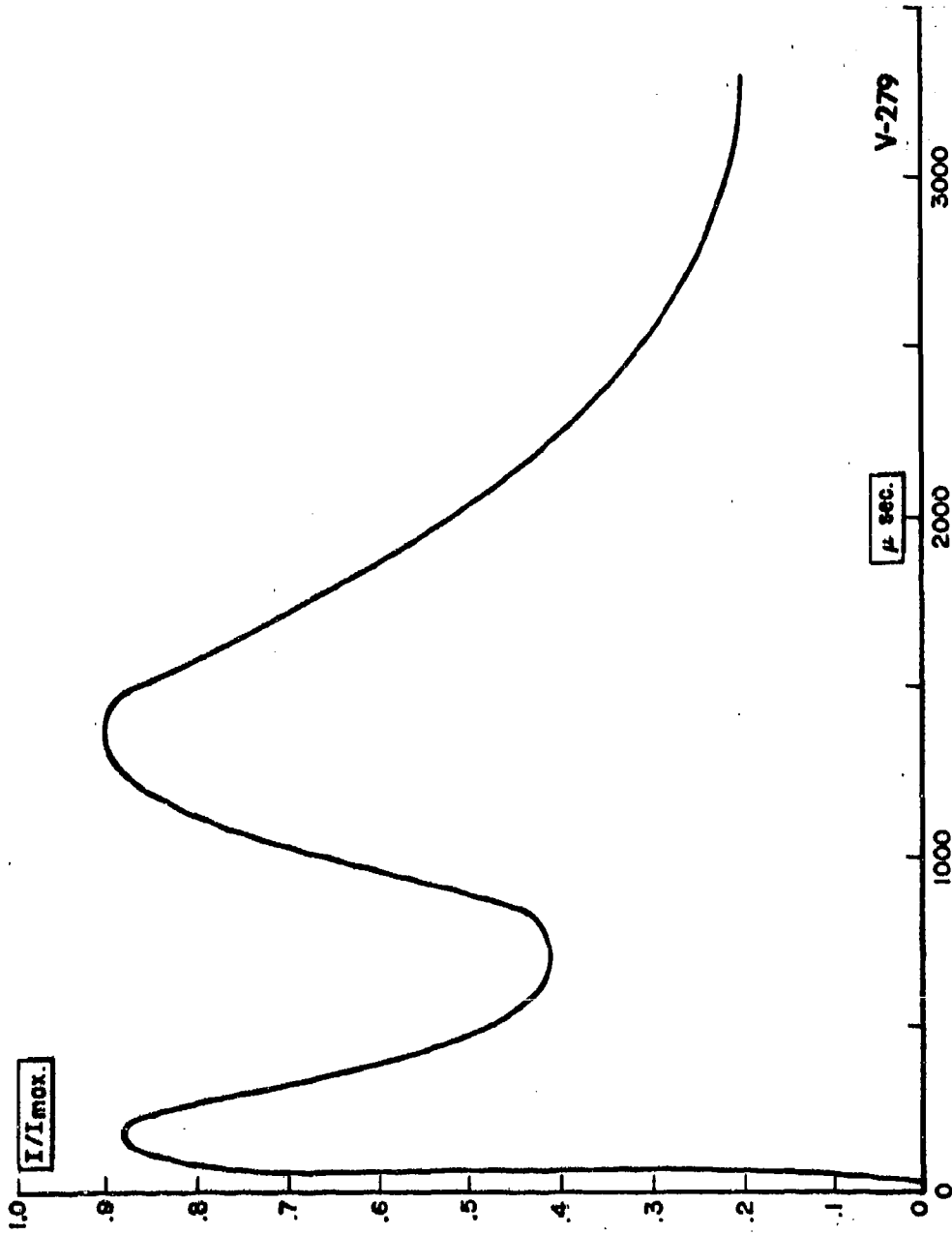
(U) Fig. 4 - Hydroxyl Radicals Observed During the Flash Pyrolysis of Boron in 20 mm Oxygen and 18 mm Water at 2000 Joules in System (ii)

-19-
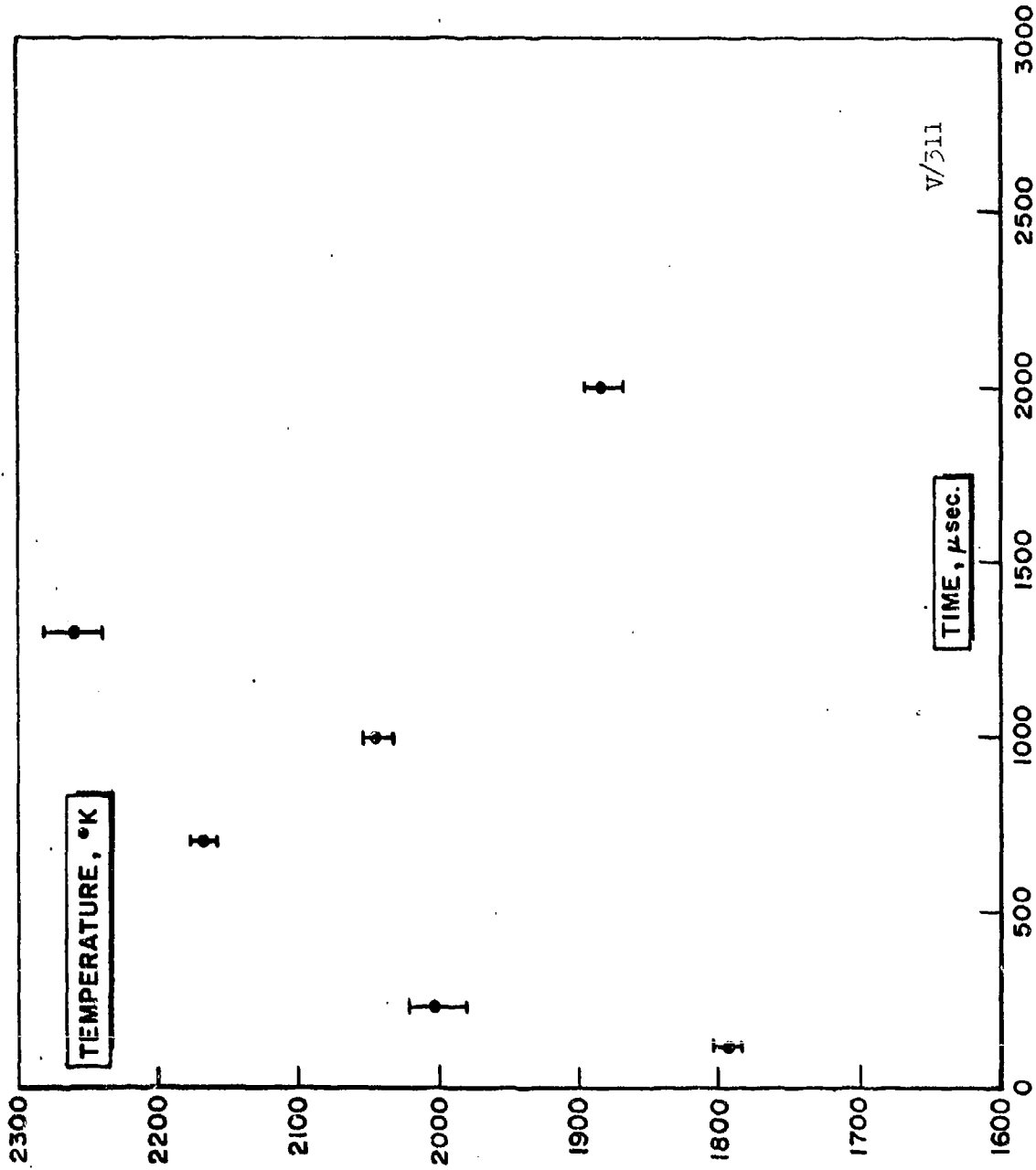
(U) Fig 5 - Flame Temperature Observed During the Combustion of Elemental Boron in Oxygen and Water in System (11)

(U) Fig. 6 – Flame Temperature Observed During the Combustion of Elemental Boron in an Equimolar Mixture of Oxygen and Fluorine in System (111)

which has twice as much fluorine as oxygen is seen in Figure 7.
In this case, maximum flame temperature is observed at 100 μsec
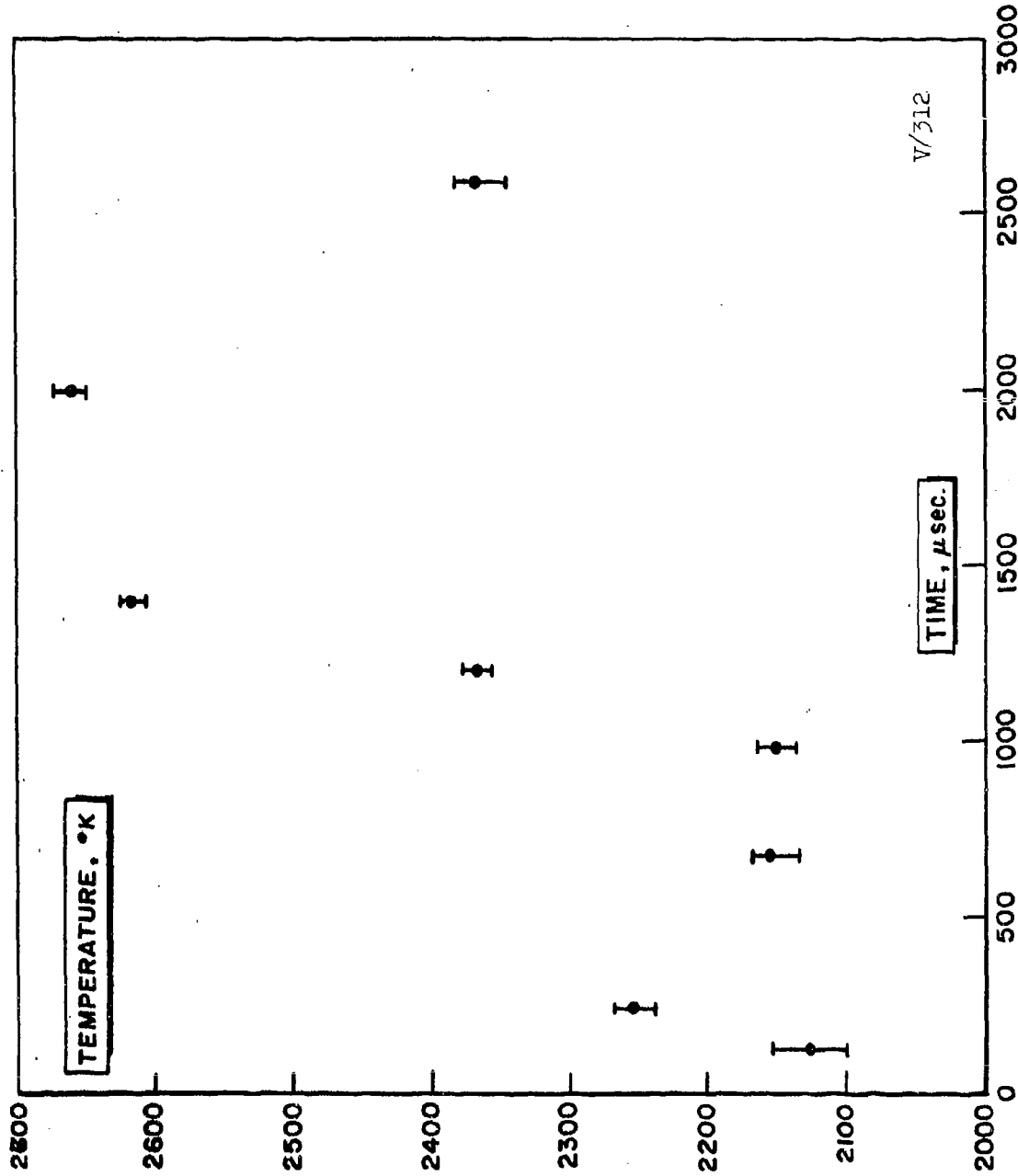(~2047°K). A minimum is reached at 500 μsec (~1730°K) and a
second maximum at 2000 μsec (~2030°K). This is considerably
below the 2633°K attained in System (iii). The flame temperature
seems to decrease as the F/O ratio is increased. The OH intensity
is about 10% of that observed in a boron/oxygen system.

(U) The overall effect of the addition of fluorine to a boron-
oxygen combustion system seems to decrease the OH concentration
with the subsequent decrease in the amount of water formed. The
flame temperature also seems to decrease as the fluorine concen-
tration is increased.

3. Combustion of Boron in Oxygen/Fluorinated Binder Prototype
    Systems   (C)

(C) The combustion of boron in 25 mm O_2 and 10 mm CH_2F_2 de-
creases the OH intensity to almost 45% of that observed when no
additive was present. The flame temperatures for this system are
seen in Figure 8. Two temperature maxima are seen; the first at
500 μsec is about 2640°K , with the second at 2000 μsec about
2515°K. These are about equal to the temperatures for a straight
boron/oxygen system. The two maxima could be indication of a two-
process flame reaction. No attempt has been made to evaluate this
phenomenon.

(C) The addition of CH_2F_2, which has the same H/F ratio as a
polyvinyl fluoride binder $(CH_2-CF_2)_x$, has very little effect on
the flame temperature of the overall combustion. It seems to mini-
mize the OH concentration, yet does not seem to prolong the com-
bustion process.

(C) The combustion of boron in an atmosphere of 25 mm O_2 and
10 mm CHF_3 was studied to determine whether the excess fluorine
of the prototype binder had a detrimental effect on the flame tem-
perature.

(U) As seen from Figure 9, the maximum flame temperature was
only ~2410°K. As in all other cases, two maxima are seen, with
the first maximum occurring at ~200 μsec. The temperature minimum
at ~500 μsec is not very pronounced and leads smoothly to the
second maximum at about 1000 μsec. The second maximum occurs
earlier than for any system studied, with exception of the fluorine-
rich System (iv), where the second maximum also occurs at 1000 μsec.

(U) The total OH intensity is about 20% of that for the boron-
oxygen system. This result and the increased BO and BO_2 intensities
suggest a scavenger effect of the fluorine atom toward the hydrogen.

(U) All studied involving the addition of fluorine-containing
molecules indicated a decrease in the amount of OH formed. The
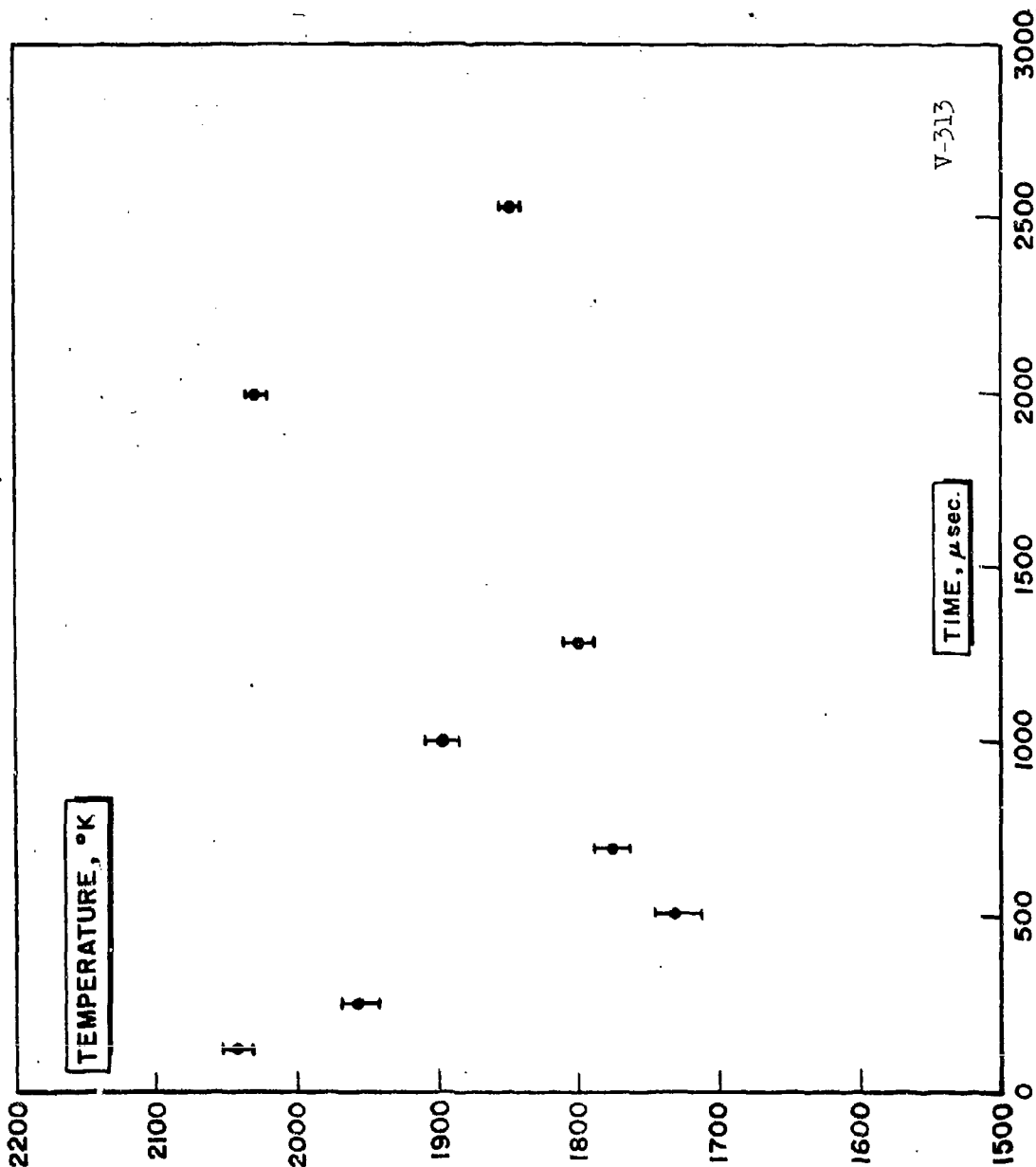
(U) Fig. 7 - Flame Temperature Observed During the Combustion of Elemental Boron in the Presence of 15 mm Oxygen and 30 mm Fluorine in System (iv)
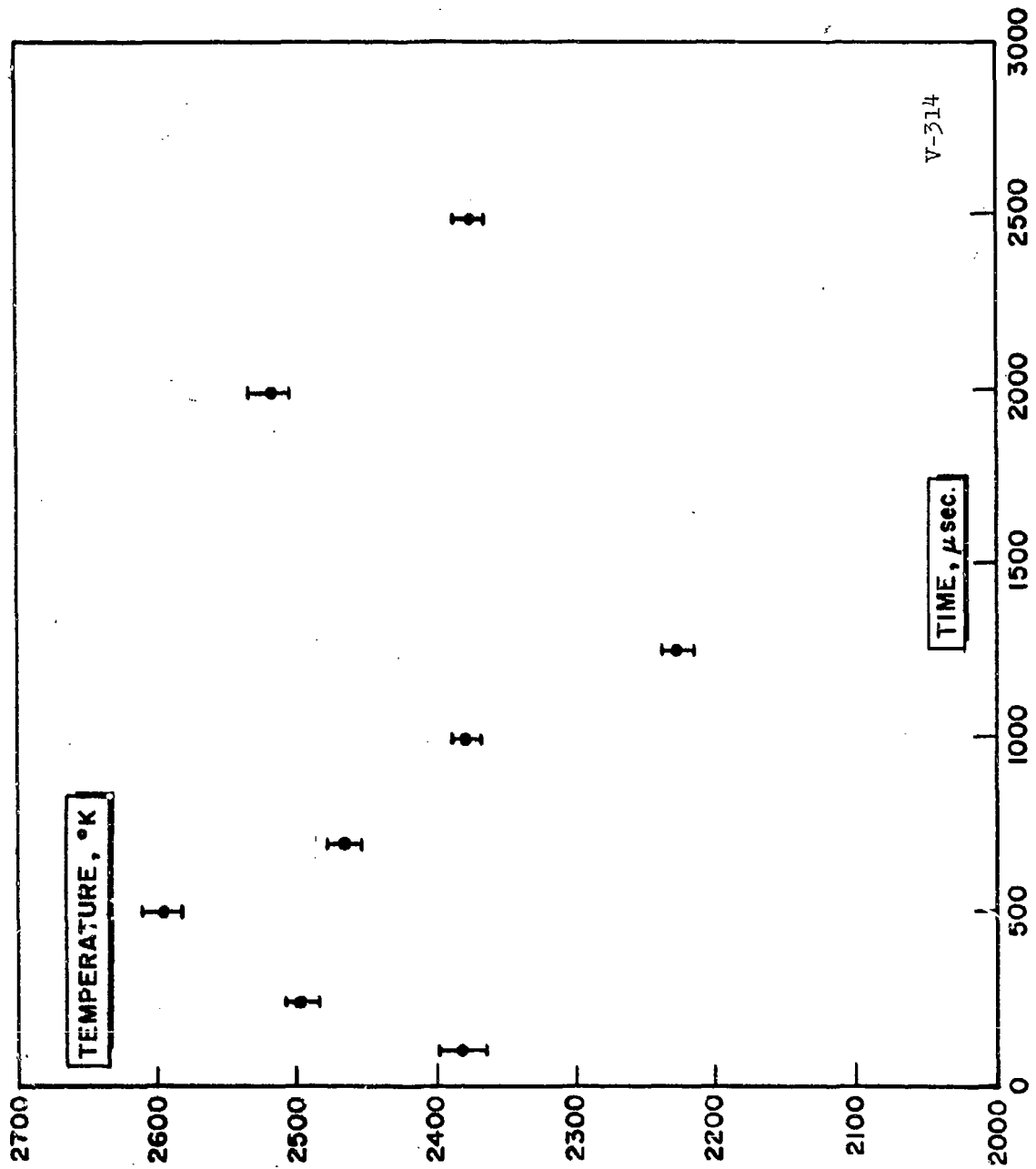
(U) Fig. 8 – Flame Temperature Observed During the Combustion of Elemental Boron in 25 mm of Oxygen and 10 mm of Methylene Fluoride in System (v)

TEMPERATURE, °K

TIME, μsec.

V-315
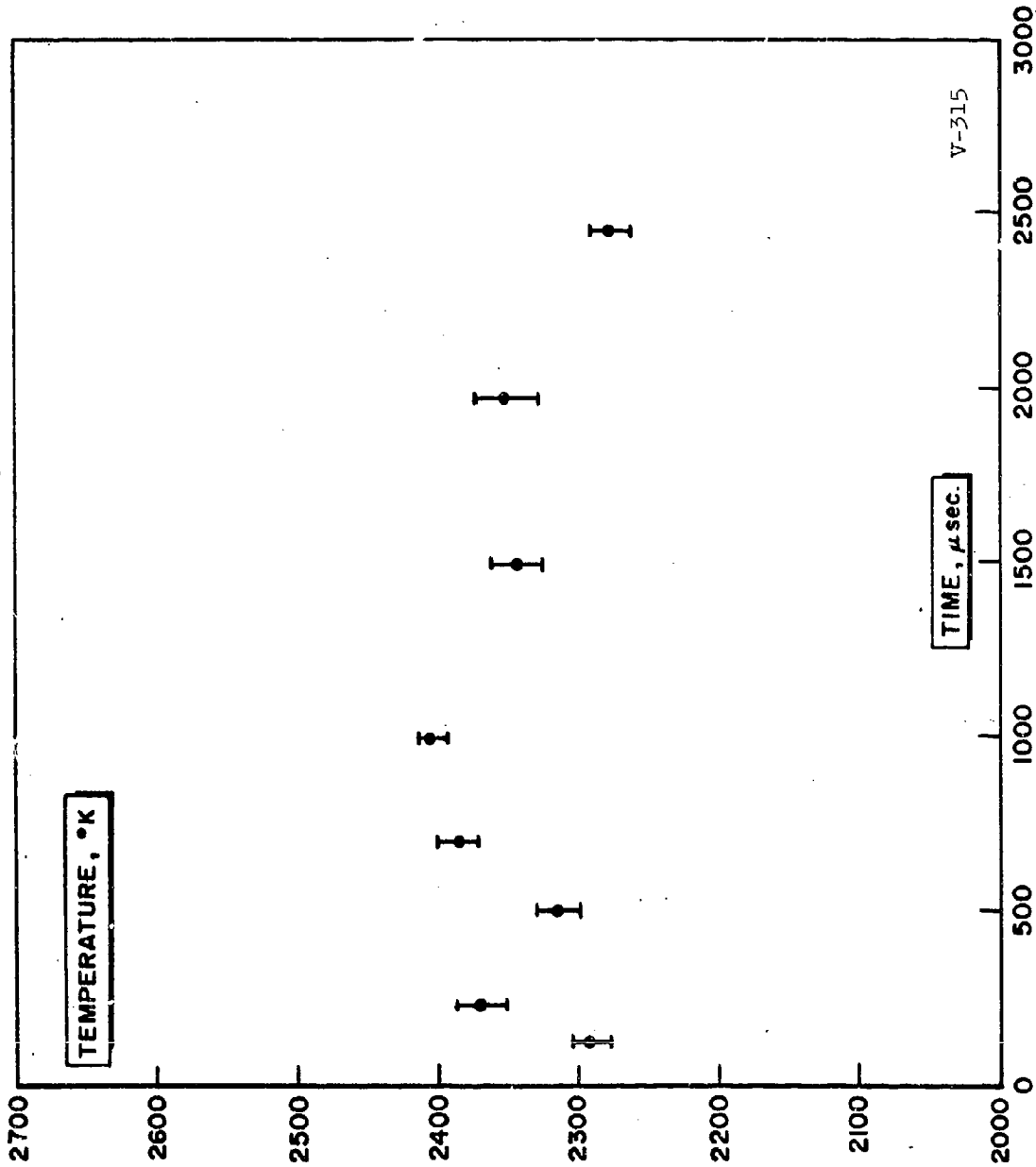
(U) Fig. 9 - Flame Temperature Observed During the Combustion of Elemental Boron in 25 mm of Oxygen and 10 mm of Fluoroform in System (vi)

initial boron products were BF and BF_3, whereas those in the last 1000 μsec were BO, BO_2, and B_2O_2, almost to the total exclusion of BF as BF_3. The final fluorine product was HF. White B_2O_3 was the ultimate condensed phase low temperature product. The major carbon species was CO, not CO_2 as postulated in Reactions (1) and (2).

D. DISCUSSION OF RESULTS (U)

1. Combustion of Boron in Oxygen and Water (U)

(U) The combustion of boron in oxygen has already been discussed in detail (31). The addition of water causes a decrease in the intensity of BO_2 and increases the intensity of OH, as expected if Equation (4):

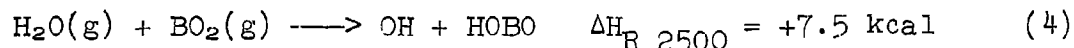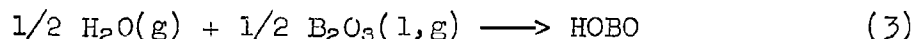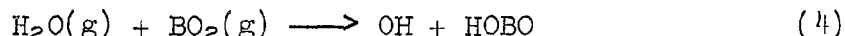$$H_2O(g) + BO_2(g) \longrightarrow OH + HOBO \qquad \Delta H_{R\ 2500} = +7.5 \text{ kcal} \qquad (4)$$

is obeyed. The endothermicity of the reaction might be a cause of the lowered flame temperature.

(U) The overall effect of the addition of water primarily lowers the ignition temperature with the subsequent lowering of the flame temperature. These two effects, along with the recognized formation of HOBO, can account for the lowered combustion efficiency of the boron AP-PBAN system. We believe the cause of this reduced efficiency is due to the large amount of H_2O found in the system. The water reacting with the BO_2 promotes the formation of HOBO at the expense of B_2O_3, the desired product.

(U) The above conclusion, if valid, immediately suggests its own remedy; reduce the formation of water in a B-AP system and the formation of HOBO will be reduced by minimizing the following reactions:

$$H_2O(g) + BO_2(g) \longrightarrow OH + HOBO \qquad (4)$$

$$1/2\ H_2O(g) + 1/2\ B_2O_3(1,g) \longrightarrow HOBO \qquad (3)$$

and

$$BO + OH \xrightarrow{M} HOBO \qquad (6)$$

The studies on the combustion of boron in oxygen and in fluorine-containing ingredients were initiated to prove the validity of this conclusion.

2. Combustion of Boron in Oxygen and Fluorine (U)

(U) The decrease in OH intensity to about 10-20% of that for the pure boron-oxygen system, coupled to the increased intensity of BO and BO_2, and the appearance of HF, indicates that

the addition of fluorine does decrease the amount of water and OH in the system. The decreased H_2O and OH seem to be due to the preferential formation of HF over these two species.

(U) The anomalous flame temperature of 2663°K for System (iii) is still a mystery (Figure 6). This flame temperature is about 100°K higher than that for a boron-oxygen flame and is almost 1000°K higher than that reported by Texaco for a pure boron-fluorine flame having $\Delta E_a = 0$ (36). The two temperature maxima seen in Figure 6 could be due to two different and separate processes. The second maximum is in the range of that for a boron-oxygen flame. It also has almost the same induction time as a boron-oxygen flame, as can be seen by comparing the rise of reaction products in Figures 1, 2, 3, and 6. The increase in BO and BO_2 concentration of Figure 1 correlates fairly well with the rise of the OH concentration of Figure 2. The shorter induction time of the maximum flame temperature of Figure 3 can also be correlated to Figures 1 and 2. The slightly longer induction time of Figure 6 can be explained as being due to the diluent effect of the HF.

(U) According to the work reported by Texaco (36), a lower flame temperature can be expected from a fluorine-rich system. This lowered flame temperature is exactly that seen for System (iv) in Figure 7. The product BF was observed to be present at times later than that observed in System (iii). This increased amount of BF could account for the lowered flame temperature, as some of the boron is not available to react with the oxygen at times less than 2000 μsec.

(U) In summary, the gross overall effects of the addition of fluorine to a boron-oxygen combustion system are:

(a) A decrease in the amount of OH and H_2O found.
(b) The final hydrogen-containing product is HF.
(c) The BO and BO_2 are seen in increased intensities.
(d) The flame temperature is decreased as the concentration of fluorine in the system is increased.

(U) From a spectroscopic point of observation, the addition of fluorine itself seems to alter the intensity of OH, BO, and BO_2 in a manner consistent with a reduction of the OH and an increase of the BO and BO_2. The flame temperature of an equivalent mixture of oxygen and fluorine is about the same as that for a boron-oxygen flame. A fluorine-rich system reduces the flame temperature.

3.   Combustion of Boron in Oxygen/Fluorinated Binder System   (C)

(C) The combustion of boron in 25 mm O_2 and 10 mm CH_2F_2 resulted in a substantial decrease in the OH intensity. The flame temperature out to 1100 μsec is higher than that for an equivalent mixture of O_2 and F_2 (Compare Figures 6 and 8). This could

be due to two causes: first, the prototype monomer CH_2F_2 has
within itself the equivalent to form 2 HF in an exothermic way;
secondly, the heat of combustion of the carbon to CO generates a
higher temperature. These two reactions probably take place
immediately ($\sim$100 μsec) after the flash. The temperature minimum
at 1250 μsec could be due to the above two reactions being final-
ized while the reaction of boron and oxygen is just beginning.
If some CO_2 were formed along with the CO, the flame temperature
would be increased above that normally expected. The formation
of CO_2 would also result in a depletion of the oxygen available
for combustion, with boron giving a lower flame temperature for
this reaction (compare second temperature maximum in Figure 8
with the flame temperature maximum in Figure 3).

(C) The flame temperature range for the combustion of boron
in a mixture of O_2 and CH_2F_2 compares favorably with that for a
pure boron-oxygen flame. The addition of CH_2F_2 does seem to de-
crease the OH and H_2O formed while still maintaining a high flame
temperature. The cause for this effect should be studied further
as it is unexpected due to the stoichiometry of CH_2F_2.

(C) The temperature of boron in 25 mm O_2 and 10 mm CHF_3, while
giving a lower flame temperature than does CH_2F_2, seems to yield
a smoother reaction as evidenced by the lesser variation in flame
temperature. The greater intensity of BF at times approaching
1000 μsec tends to indicate that some of the fluorine originally
present in the CHF_3 would be available to scavenge the hydrogen
from the NH_4ClO_4 and form additional HF directly or by a reaction
similar to Reaction (3).

$$2\ BF_3(g) + 3\ H_2O(g) \longrightarrow B_2O_3(g) + 6\ HF(g) \qquad (3)$$
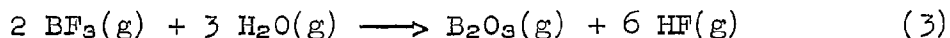
(C) The flame temperature of the $B/CHF_3/O_2$ system is inter-
mediate between that for $B/CH_2F_2/O_2$ and 2 $F_2/O_2/B$. Again, the
indication is that the more fluorine that is added to the system,
the lower is the flame temperature.

(C) We believe that we have demonstrated, from a combustion
point of view at least, that certain prototype fluorinated monomers
are helpful in reducing the amount of OH and H_2O present during
the combustion of boron in a system containing oxygen and hydrogen.
Furthermore, we believe that a binder which contains just enough
fluorine to give HF stoichiometrically when all the hydrogen in
the system is reacted will yield a flame temperature comparable
to that of pure boron-oxygen flame.

E. RECOMMENDATIONS (U)

(C) We recommend that additional work be performed to pursue
more intensively the use of fluorinated binders for air augmented
boron-containing solid rocket propellants. The work reported
above shows that it may be possible to minimize the formation of
HOBO by reducing the OH and H_2O in the combustion system by the
addition of certain fluorinated binders.

F. FUTURE WORK (U)

(U) The remainder of the year will be spent on studying the combustion reaction of aluminum with O_2, H_2O, Cl and mixtures of the above. Work will also continue on the reaction of boron with NH_4ClO_4, with and without the presence of H_2O and F_2.

SECTION III

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13 ABSTRACT

The heat of formation of CF_4 was derived as -223.2 ± 0.6 kcal /mole from measurements of the heat of explosion of mixtures of C_2N_2 and NF_3, in good agreement with recent work from other laboratories. The heat of formation of CF_3ONF_2 was calculated from the heat of explosion data as -189.1 ± 0.8 kcal /mole. This result implies a relatively strong bond energy $E(N-O) = 53$ kcal./mole, contrary to some evidence indicating $E(N-O) = 35$ kcal./mole. Recalculations of the data previously obtained on Beane and ATBH now show a higher precision. The heats of formation were slightly revised as follows: Beane, from -5.3 to -5.0 kcal /mole; ATBH, from -33.7 to -35.7 to -35.7 kcal /100 grams. Work on DAHTP, Florox, and other compounds is in progress. The preparation of pure, solvent-free TVOPA has been completed and it has been determined to contain only negligible benzene residue. The photochemical process previously used to prepare CF_3NF_2 has been replaced by a process involving low temperature fluorination of KSCN. This process reduces side products and simplifies purification. The flash pyrolysis of boron has been studied in the presence of oxygen, fluorine and two prototype monomers. The studies are aimed at minimizing the formation of OH and H_2O and thereby, hopefully, that of HOBO in an air augmented system. Flame temperatures of the various combustion systems are discussed as well as the change of OH concentration. The concentration of OH and H_2O, and thus the amount of HOBO are decreased by the addition of elemental fluorine as well as the two prototype monomers CH_2F_2 and CHF_3, thereby increasing the combustion efficiency of a boron-fueled air augmented system.

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